ISOTOPES AND RADIATION TECHNOLOGY

A Quarterly Technical Progress Review

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Isotopes and Radiation Technology

is a Technical Progress Review prepared by the Isotopes Information Center, Oak Ridge National Laboratory, at the request of the Divisions of Technical Information and Isotopes Development, U. S. Atomic Energy Commission. This Review is intended to assist those interested in keeping abreast of significant developments in the fields of isotopes and radiation technology. It is not a comprehensive review of all literature published in this field during a given quarter; rather, it is a mechanism for presenting concise, selected reviews of information on subjects of prevailing Commission interest as it becomes available.

This Review attempts to relate the published results of research and development sponsored by the Division of Isotopes Development to significant developments in radioisotopes and radiation technology, as reported in the world literature. Coverage includes isotope production and development, isotope technology development, isotope applications technology, process radiation development, and radiation processing of food and medical supplies.

In addition to reviews of current literature and special review articles dealing with specific isotopes, facilities, and applications, this publication occasionally contains feature articles prepared by recognized experts on specific topics of current interest. Critical evaluations and interpretations presented are those of the editors and invited reviewers; therefore readers are encouraged to consult the original references in order to obtain all the background of the work reported and the interpretation of the results given by the original authors.

The subject headings listed below have been adopted to help maintain continuity and order, from one issue to the next, in the material reviewed. All reviews, except Feature Articles, will be arranged under these headings; but any one issue will not necessarily contain all the headings.

Isotope Production and Development
Isotope Technology Development
Food Irradiation
Process Radiation Development
Source Development
Isotopic Power Development
Applications in Life Sciences
Safety
Isotopes Around the World
Miscellaneous

P. S. Baker, Robert H. Lafferty, Jr., Martha Gerrard, R. E. Greene, F. E. McKinney, Joan E. Carden, and F. J. Miller, *Editors*
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Oak Ridge National Laboratory

Section I

Isotopes and Radiation Technology

General Review

The AEC's Program in Industrial Applications of Radiation and Radioisotopes*

By William E. Mott† and George J. Rotariu‡

Abstract: The primary objective of the Division of Isotopes Development's industrial applications program is to induce advances in radiation and radioisotopes technology leading to economic industrial applications in the public interest. A secondary objective is to increase the number and scope of specific practical applications so that industry will have as broad an opportunity as possible to start profitable ventures. We hope we are complementing rather than duplicating outside efforts. The decision to support a proposed industrial application—technique, instrument, or process—rests largely on the value or advantage the end product of the proposed effort would have over existing methods or practices.

Each day, we, the consumers of this nation, open 70 million cans of assorted food products. This is equivalent to an annual consumption of 145 lb per person, or a total consumption of nearly 28 billion lb/year. In addition, we now consume 3.7 billion lb of frozen fruit and vegetables per year. Considering the large quantities of food involved and the widespread use of pesticides and detergents to improve food quality, the country's food processors have had to solve some very severe cleansing problems in order to achieve requisite standards of food purity. Three years ago the AEC initiated a joint program on pesticide- and detergent-residue control with the National Canners Association to determine, by the use of radiotracers, the best methods of cleaning enormous quantities of foodstuffs. This objective has been successfully met, and the results and conclusions of the studies have been disseminated to, and adopted by, the food-processing industry.[1] I have opened with this example because, to me, it spotlights one of the most important, yet least publicized, areas in the industrial radiation and radioisotope applications business—the one-shot use of radioisotopes (or radiation) to develop or improve industrial practices and processes that are otherwise unrelated to radioisotopes. The economic impact of such applications, which usually occur without much fanfare, can seldom be recorded directly; nevertheless, the role they play in our economy should not be underestimated.

As these comments imply, my intention is to discuss industrial applications of radiation and radioisotopes. Specifically, I will be discussing those applications in which the Division of Isotopes Development (DID) is interested. Major areas to be covered are the Analysis, Evaluation, and Control Program; the Radiation Preservation of Foods Program; and the Process Radiation Program. Before turning to these subjects, however, a word should be said about the origin and value of the radioisotopes that are used in present-day applications.

As most of you probably know, DID has the responsibility within the Commission for determining the radioisotope requirements for the country and for ensuring that these requirements are met. During the early years of the isotope program, the demands of users and customers were fulfilled by the Oak Ridge National Laboratory. In August 1952, procedures for importing radioisotopes into the United States from Canada were simplified, with the result that in 1965 Canada exported $1.6 million worth of isotopes to the United States. In 1965 the total value of imports was $2.8 million from 15 countries.

Commercial production of radioisotopes in privately owned reactors began in about 1959. As a direct result of this commercial availability, the AEC has withdrawn from the routine production and distribution of 36 different radioisotopes since 1961.§ The Bureau of the Census recently reported that the value of radioactive isotopes shipped from non-AEC plants producing radioisotopes had grown to $4.4 million in 1965. Shipments of about 10 million curies

*Presented at the Winter Meeting of the American Nuclear Society, Pittsburgh, Pa., Nov. 3, 1966.

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§Since the talk, AEC has withdrawn from the production of ^{87m}Sr generators.

of processed radioisotopes have been made to date from Commission laboratories; an additional 2 to 3 million curies have been imported; and about 1 million curies have been commercially produced. An estimated U. S. market of another 10 to 12 million curies over the next 2 years is now being forecast. A major fraction of these curie quantities is for ^{60}Co, and the requirements for this key isotope will continue to increase because of increased emphasis on the food-irradiation and process-radiation programs. The demand for fission products also continues to increase.

Analysis, Evaluation, and Control

The work on determination of insecticides and detergents in food mentioned above is typical of that which goes on in DID under the Analysis, Evaluation, and Control Program. Our aim is to assist on problems whose solutions will broadly benefit a particular industry but which are not likely to be promptly attacked by individual companies in that industry.

POLLUTION

On the subject of pollution, the Division's interest goes back to a radiotracer study of sewage flow rates in the vicinity of El Segundo, Calif., in 1958. Between 1958 and 1965 the Division supported two projects in pollution control, of industrial interest—the development of a device to monitor sulfur dioxide and ozone in the air[2] and the development of a radioisotope gage to measure amounts of suspended solid particles carried downstream by rivers.[3] Current work being sponsored by DID includes a cooperative project with Washington State University and three paper and pulp mills, aimed at developing means of identifying how much pulp waste each company is discharging into local streams. The method employed consists of tagging the wood pulp with an inert chemical tracer that adheres to the wood fibers, such as lanthanum. Samples of water, taken from plant effluents or from streams into which the effluents flow, are activated in a nuclear reactor; and the tracer, and hence the pulp pollutant, is identified and determined by gamma-ray spectroscopy.

Equally important is a project now in the pilot-plant stage to determine the efficiency of chromium removal by ion exchange from chromium-plating solutions. The approach is to add minute quantities of ^{51}Cr to the plating baths. When the capacity of the ion-exchange columns to remove chromium from the spent bath is exceeded, radioactivity is detected in the effluent from the columns, and the solution is then automatically routed to fresh ion-exchange columns. Thus the amount of chromium that is inadvertently dumped into sewers can be reduced to a negligible quantity. This procedure will contribute to a reduction in the contaminants fed to streams in industrial waste water. If the process should prove to be economically attractive, it is hoped that most chromium-plating works will soon take steps to install the necessary equipment.

One of the most important problems in air pollution today is that of sulfur dioxide. Significant amounts of SO_2 are introduced into our atmosphere primarily through the burning of coal—the sulfur content of bituminous coal ranges from 0.5 to 6%, with an average value of 2.5%. For example, a 150-Mw(e) utility plant may burn some 75 tons of coal per hour, with each ton of coal burned producing about 400,000 cu ft of total gases containing about 0.3 wt.% SO_2. Analytical methods are needed for (1) continuously monitoring the SO_2 content of effluent stack gases, (2) measuring the distribution of the stack-gas plume over the neighboring areas, and (3) determining the sulfur content of coal on rapidly moving belts. DID is starting a program to help solve the first two problems. Concerning the determination of the sulfur content of coal, progress has been made by one of our contractors, who is investigating tritium-excited X-ray-fluorescence analysis. In fact, preliminary calibration curves of X-ray counting rate vs. sulfur content are of sufficient quality that analysis by the X-ray-fluorescence method appears entirely feasible.

ACTIVATION ANALYSIS

Since 1958 our Division has spent more than $2 million on basic and applied work with neutron activation analysis. The basic technology has now become quite firmly established so that we are currently concentrating our support on applied areas. Our main efforts have been aimed at accelerating the application of the activation technique to process-stream analysis and control.[4] For example, successful tests with neutron generators have indicated applicability to the on-line determination of ash content and calorific value of coal and trace elements in aluminum ore. Future work planned includes the evaluation of the method for analysis of fertilizers and chemicals, as well as of slurries in a liquid loop. Industrial firms with an interest in the analysis and control of process streams are invited to participate in the use of the joint AEC–industry test facility at Austin, Tex.

Radiation Preservation of Foods

Let us now focus attention on an area that has one of the largest volume potentials for industrial irradiation—food. The U. S. Radiation Processing of Foods Program has two distinct, but parallel, efforts. The first, under the direction of the Department of the Army,[5] is concentrating on the radiation sterilization of meats, e.g., ham, pork, chicken, and beef, which are of special significance in the shelf-stable military ration. After sterilization by radiation, packaged meat can be held indefinitely, in good quality, at ambient

temperatures. The other phase of the national program is carried out by the AEC.[6] The objective under this program is to develop radiation-pasteurization techniques wherein the fresh shelf life of foods such as fruits and marine products can be extended significantly, with resultant reductions in spoilage and extension of marketing times.

We have now entered the phase of the pasteurization program where commercial participation and interest in certain specific food products should result in limited commercialization before the end of the 1960's. Of course, the critical requirement is and will continue to be the clearance of each product for public consumption by the Food and Drug Administration (FDA).[7,8] Interestingly, a number of individual food companies are actively cooperating with AEC in carrying out important program aspects that must precede commercial use. For example, commercial transportation channels have been used to send irradiated and nonirradiated haddock fillets to principal seafood buyers of interested chain stores and other industry members located hundreds of miles away from our irradiator at Gloucester, Mass. The fillets have been tested by experienced people under commercial quality-control conditions. Eight major food chains have participated in these tests, and all have reported that the irradiated fillets continue to be acceptable for 6 to 14 days after the nonirradiated fillets are no longer marketable. These chains envision that irradiation will reduce waste, increase profits, and enable them to pass savings along to consumers.

Twelve irradiator units[9] are used in the AEC's Food Irradiation Program. We continue to offer the services of these facilities to companies that want to conduct their own tests. In return, they make their data and information available to us. As a further method of involving the food industry, we plan to use a portable cesium irradiator, which will be operational in early 1967, for on-site irradiation of products of interest to particular companies. In return for the use of this portable irradiator, the companies will provide us with the results of their tests. In developing a "use" schedule, first priority will be given to companies that are processing products for which clearance has already been granted by the FDA, or has been requested.

Thus much of our effort is directed toward the commercialization aspects of irradiated food. Within the same area , some of the Army's procurement plans that have recently been completed or announced are:

1. Thirty thousand pounds of radiation-sterilized bacon were procured in June and July 1966.
2. Four hundred thousand pounds of irradiated white potatoes were to be procured during the winter of 1966.
3. Two hundred thousand pounds of radiation-sterilized ham will be procured in FY 1967, or as soon as FDA and USDA clearances are obtained.
4. One hundred thousand pounds of pasteurized marine products will be procured following FDA clearance.
5. Two hundred thousand pounds of irradiated wheat flour will be procured during FY 1967.

From these examples a definite trend is evident: Food irradiation is on the way to becoming a commercial reality.

Process Radiation

Interest by DID in the development of process radiation is well known; the Process Radiation Development Program was started in 1958. The primary objective of this program is to put ionizing radiation to work in our economy.

An application now approaching commercial reality is the radiation production of wood–plastic materials.[10] This product is a combination produced by impregnating wood with a liquid monomer, such as methylmethacrylate, and then irradiating the composite to induce polymerization. The result is a material, which, compared with natural wood:

1. Is harder by several hundred percent and thus more resistant to blows, scratches, etc.
2. Has much higher compression strength and abrasion resistance
3. Absorbs moisture more slowly and therefore has more dimensional stability (resistance to warping and swelling)
4. Has much improved shear and static bending strength

In addition, it retains the natural wood grain and color, or can be artificially colored throughout, and can be sawed, drilled, turned, and sanded with commercially available equipment, giving a hard, beautiful, satin-smooth finish.

This family of material shows promise for use in a wide number of applications, including, but not limited to, furniture, floors, window frames, sills, and doors; tool handles; musical instruments; sporting goods; boat decks and fittings; and dies and jigs. Two commercial firms are now producing and marketing wood–plastic material, and several others have the process under consideration. The total present production capability in this country is about 1.0 million lb/year.

Another radiation process now approaching commercial utilization is the production of polyethylene by replacing conventional catalyst systems for both high- and low-density polyethylene with ionizing radiation. At least six advantages are envisioned:

1. Elimination of catalyst impurities in the product
2. Better control of the rates of production during operation
3. Better control of molecular-weight distribution during operation
4. Production of both high- and low-density polyethylene in a single plant by altering process conditions

5. Elimination of catalyst pumps and injection equipment

6. Ability to produce copolymers of ethylene without extensive modification of catalyst systems

At least one private company is now entering a pilot-plant study of the process, and several others have initiated serious laboratory-scale investigations.

Two other processes developed by the AEC are now being considered for "commercialization." These are the fabrication of semiconductor components using transmutation doping techniques and radiation-induced emulsion polymerization.

The transmutation doping technique consists of producing, by neutron bombardment, electronically active impurities in germanium or silicon in a special pattern defined by slits photoetched in cadmium.[11] Although the process is still under development, the basic technology of transmutation doping has now been mastered. Each of the individual electronic components used in microcircuits—including transistors, diodes, resistors, and capacitors—has been made by transmutation doping. All show acceptable electronic properties. Several simple microcircuits have been made. The potential economics of the process appear promising, particularly for small-lot production and for items that cannot be fabricated by current techniques. The step from simple component fabrication in unfinished form to microcircuit fabrication in relatively finished form is being taken in the current phase of our development program.

The radiation-induced emulsion polymerization program is primarily aimed at developing a process to produce latex materials used in water-base paint formulations. Because the radiation process can operate efficiently at low temperatures (0°C), the product has a much higher molecular weight than the conventionally produced material. This higher molecular weight imparts greater wear properties to the paint film. An additional advantage of the radiation process is precise control over free-radical initiation. Catalyst or excess monomer residues—a problem with conventionally produced latex—is not a factor with the radiation-induced polymerization reactions. The economic and practical feasibility of using this process on an industrial scale is now under study. (RHL)

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Section II

Isotopes and Radiation Technology

Isotope Production and Development

Transuranium-Element Processing

By D. E. Ferguson*

Abstract: The chemical processing scheme and the design of the facility for processing the transuranium elements at Oak Ridge National Laboratory are described.

The Transuranium (TRU) Facility at Oak Ridge National Laboratory (ORNL) was designed for chemical processing and handling of materials containing the highly radioactive heavy isotopes beyond uranium in the Periodic Table. These elements (Table 1) not only are useful in basic physical and chemical research but also have practical applications. For example, the alpha-emitting nuclide ^{244}Cm is used as a heat source in direct-conversion devices to provide electrical energy to power man-made earth satellites and space probes. Californium-252 undergoes spontaneous fission to produce neutrons and so is potentially useful as a portable, reliable neutron source.

Table 1 PROPERTIES OF SOME IMPORTANT TRANSPLUTONIUM ISOTOPES

Isotope	Type of radiation	Half-life	Neutrons, n/(sec)(g)	Specific power, watts/g
^{244}Cm	Alpha	18.1 years	1.1×10^7	2.83
^{249}Bk	Beta	314 days	3.4×10^5	1.1
^{249}Cf	Alpha	360 years	4.5×10^5	0.14
^{250}Cf	Alpha	13.2 years	1.2×10^{10}	4
^{252}Cf	Alpha	2.65 years	2.3×10^{12}	38
^{254}Cf	Fission	60.5 days	1.2×10^{15}	11,000
^{253}Es	Alpha	20 days	3.1×10^8	1000
^{254}Es	Alpha	480 days	1.3×10^9	41
^{254}Fm	Alpha	3.24 hr	3.5×10^{14}	170,000
^{255}Fm	Alpha	21.5 hr	1.6×10^{10}	25,000

These nuclides will be produced in the ORNL High Flux Isotope Reactor (HFIR). The HFIR has a remarkable power density—1 Mw per liter of core volume when operating at full power—and a peak thermal flux of 5×10^{15} n/(cm^2)(sec) in the central moderator region.

The production of the heavy elements starts with ^{242}Pu (Fig. 1). Ten successive neutron captures, interrupted by beta decays from one element to the next, are required to produce ^{252}Cf. Therefore the production rate is very sensitive to neutron flux, and the thermal-neutron flux required to make significant amounts of the transplutonium isotopes in a reasonable time (tens of milligrams of ^{252}Cf per year and larger amounts of the lighter nuclides) is about 2 to 5×10^{15} n/(cm^2)(sec). By irradiation of 10-kg batches of ^{239}Pu in the Savannah River plant reactors, several hundred grams of ^{242}Pu and smaller amounts of ^{243}Am and ^{244}Cm were produced in a few years. In the TRU facility this americium–curium is being isolated for reirradiation in the HFIR; the targets from the HFIR irradiation programs will be processed to obtain the desired heavy elements and to recover the unused target substances; and numerous other procedures will be carried out on highly radioactive materials.

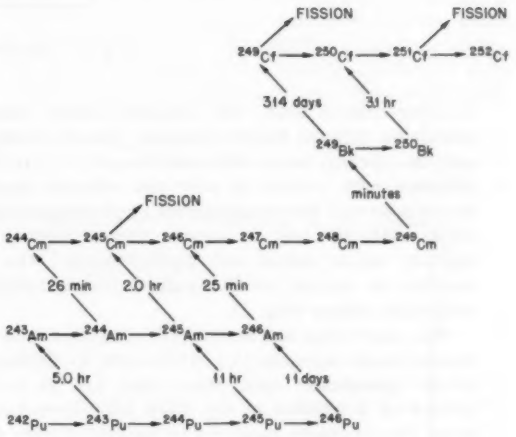

Fig. 1 Production of heavy elements from ^{242}Pu.

Chemical Processing of HFIR Targets

The first step in processing (Fig. 2) of the HFIR targets is dissolution of the aluminum-clad targets

*Chemical Technology Division, ORNL.

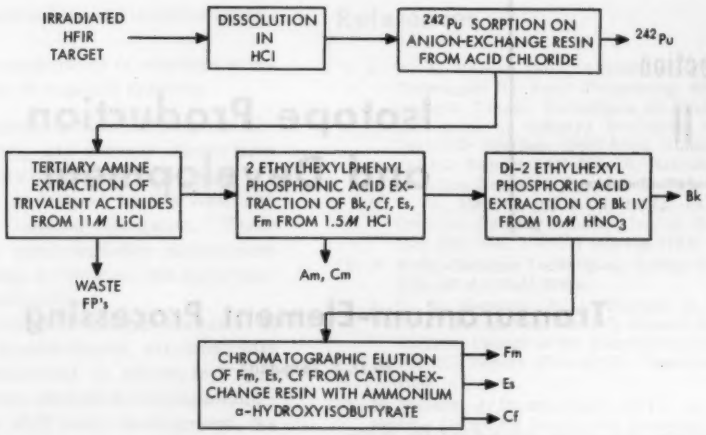
IRRADIATED HFIR TARGET
DISSOLUTION IN HCl
^{242}Pu SORPTION ON ANION-EXCHANGE RESIN FROM ACID CHLORIDE
^{242}Pu
TERTIARY AMINE EXTRACTION OF TRIVALENT ACTINIDES FROM 11M LiCl
2 ETHYLHEXYLPHENYL PHOSPHONIC ACID EXTRACTION OF Bk, Cf, Es, Fm FROM 1.5M HCl
DI-2 ETHYLHEXYL PHOSPHORIC ACID EXTRACTION OF Bk IV FROM 10M HNO_3
Bk
WASTE FP's
Am, Cm
CHROMATOGRAPHIC ELUTION OF Fm, Es, Cf FROM CATION-EXCHANGE RESIN WITH AMMONIUM α-HYDROXYISOBUTYRATE
Fm
Es
Cf

Fig. 2 Chemical processing of HFIR targets.

in hydrochloric acid. The solution, which contains aluminum, unused target material, fission products, and the several heavy elements desired, is carefully adjusted with respect to acid and chloride concentrations so that the transuranium elements are selectively extracted into an organic solvent mixture—a tertiary amine mixed with diethylbenzene. The extraction is carried out in a pulsed column contactor with many stages (Fig. 3).

The americium and curium are extracted from the transuranium-element fraction with 2-ethylhexylphenyl phosphonic acid. Since they are to be returned as a mixture to the HFIR for reirradiation, these two elements need not be separated from each other. Berkelium is isolated next, after being oxidized to the highly extractable tetravalent form. Finally, californium, einsteinium, and fermium are separated by ion exchange in a procedure similar to that used for separating rare-earth elements. All these operations require highly specialized equipment and instrumentation since they must be carried out in a sealed cubicle shielded from the operators by 4.5 ft of high-density concrete.

The additional purification needed for the ultra-high-purity materials required for research will be accomplished in small glass equipment to avoid contamination of the products by equipment corrosion. Again, a heavily shielded, sealed cubicle is required to protect the operators.

The equipment for americium–curium target fabrication is remotely operated. The americium–curium mixture is first converted to oxide microspheres. This oxide is then mixed with powdered aluminum and pressed into a pellet, and the pellets are inserted in an aluminum tube, which is welded closed to form the irradiation target. The same equipment and procedure will be used to prepare other highly radioactive elements, such as califor-

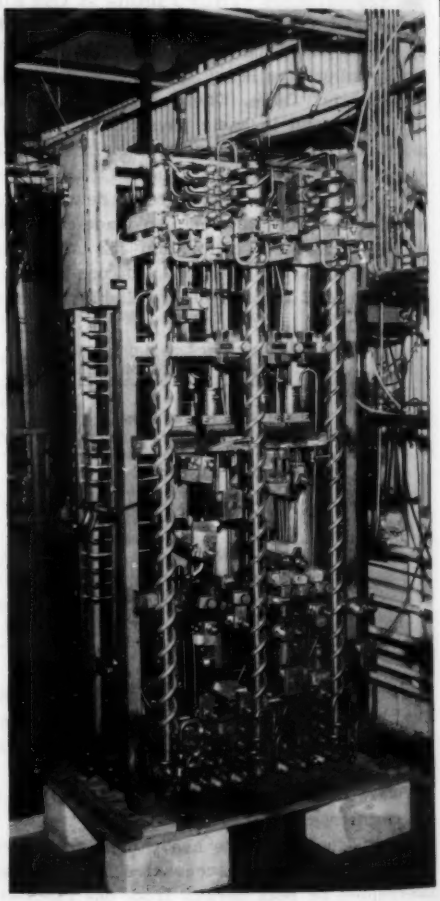

Fig. 3 Solvent extraction equipment rack.

nium, for irradiation in the HFIR; large quantities that are to be shipped will also be encapsulated.

TRU Facility Design

The TRU Facility (Fig. 4) has nine cells arranged in a line, eight laboratories, and space for necessary auxiliaries. Each cell has a viewing window and master–slave manipulators (Fig. 5). Two cells are used for chemical analysis of highly radioactive solutions for process control. Four cells are used for chemical processing; three of these contain the main line of process equipment, and the fourth is used for special separations to prepare the ultrahigh-purity transuranium elements needed for research. Two more cells are provided for making irradiation targets for the HFIR and for packaging transuranium elements for shipment. A final cell is used for inspection of HFIR targets before they are shipped to the reactor. The laboratories are equipped for handling alpha-active materials not requiring heavy concrete shielding and are used for chemical analysis and laboratory development work with these active materials.

The cells have 4.5 ft of magnetite-concrete shielding, chosen for its high iron and water contents, which in combination are effective in stopping the high-energy spontaneous-fission neutrons emitted by the transuranium elements and the gamma radiation resulting from the neutron captures in the shield. The cells are separated from one another by 2 ft of concrete shielding, which allows maintenance or alterations in one cell without extensive cleaning of the others. An alpha-tight cubicle was installed at the viewing-window level to contain the very hazardous materials to be handled. There are four separate air-cleaning systems: a process-vessel vent system complete with a scrubber and three absolute filters in series; a cubicle-ventilation system, which recirculates air from the cubicles through an elaborate air-conditioning and cleaning system; a cell-ventilation system, which passes air through the cells

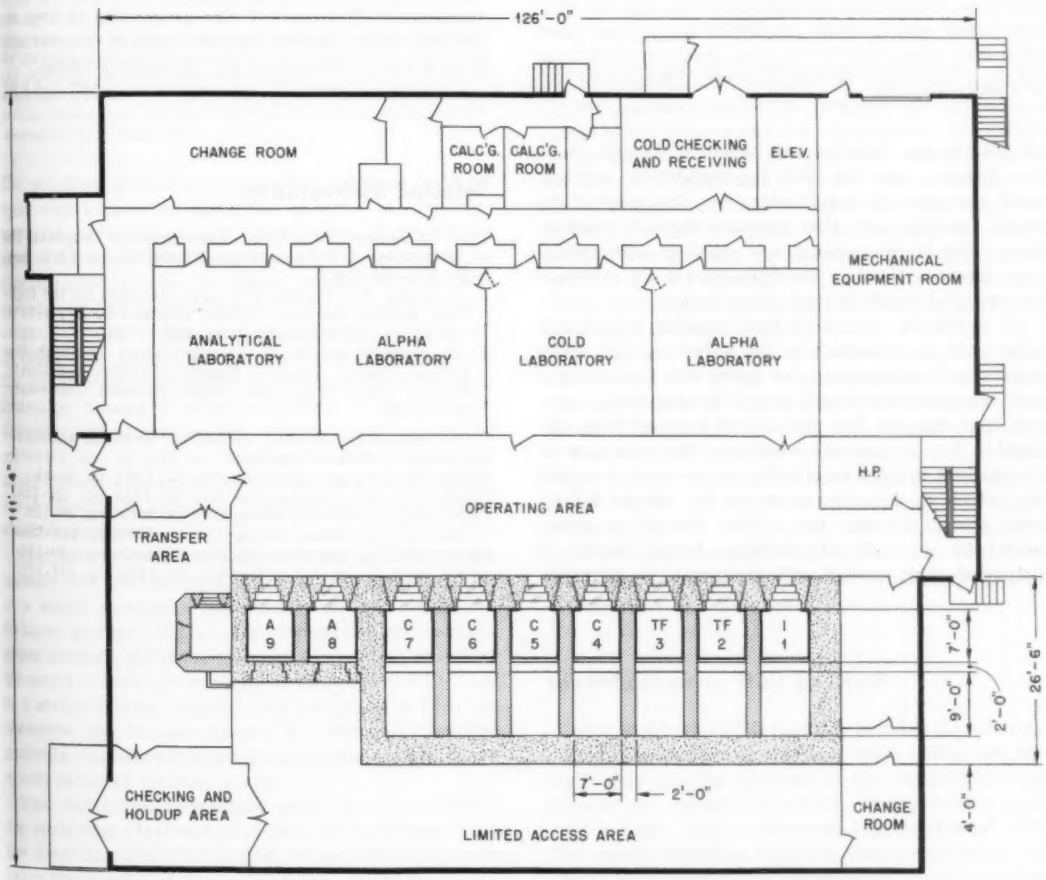

Fig. 4 Plan of first floor of TRU Facility.

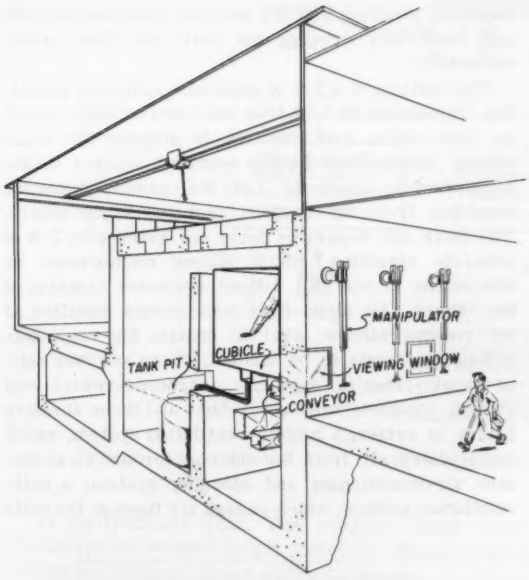

Fig. 5 The TRU processing facility, showing cross-section of a processing cell.

but outside the cubicles and exhausts through absolute filters; and the building-ventilation system, which provides air conditioning for the inside of the sealed building and also exhausts through absolute filters. All these systems are equipped with radiation detectors to warn the operators if any radioactive material starts to leak to the outside.

All operating equipment that requires repair and adjustment is enclosed in the cubicles, and these repairs and adjustments are made with the master–slave manipulators. Small pieces of equipment, samples, and supplies are put into or removed from the cubicles by an intercell conveyor. The conveyor is so designed that the materials are moved in a sealed can, which in turn is sealed to the cubicle before being opened so that the sealed cubicle is never opened to the cell atmosphere. Large pieces of equipment contaminated with transuranium elements are removed from inside the cubicles by a sealed, shielded caisson. This caisson is operated from above after blocks of concrete shielding over the cells have been removed. The principle of containment is the same as that of the conveyor, and the cubicle is never opened to the cell atmosphere in removing or replacing defective equipment.

Behind the cubicle in each cell is a deeper cell space for the tanks and process vessels, which normally require little maintenance.

The TRU Facility processing equipment is small since the amounts of materials handled can be measured in grams. Routine maintenance is done with master–slave manipulators, and all equipment is replaceable by remote means. If required, the cells can be stripped completely, including the service pipes and electrical wiring, without exposing either the cell interior or the used equipment to the atmosphere.

In the four cells where the chemical separations are made, the equipment is made of tantalum or Zircaloy-2 to resist corrosion by the chloride solutions used. This part of the processing is done on a 20-liter scale, and the complex system includes more than 3 miles of tantalum and Zircaloy-2 tubing.

(MG and RHL)

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ORNL-3945, for period ending May 31, 1966, pp. 107-128.

Section III

Isotopes and Radiation Technology

Isotope Technology Development

Forensic Applications of Neutron Activation Analysis

By W. S. Lyon and F. J. Miller

Abstract: The sensitivity and nondestructiveness of neutron activation analysis have made it an attractive technique for forensic scientists. Much work has been done on the unique identification of individuals by hair comparison. Information has been obtained as to normal and abnormal levels of trace elements in hair. The many possible sources of error in the procedure are discussed, and the necessity for establishing a firm scientific basis for identification is shown. Other possible areas of neutron activation analysis use in the identification of various materials as to origin are cited and discussed briefly. The availability of neutron activation analysis services for law-enforcement agencies and for private individuals is listed, and the costs of equipping a NAA laboratory are reviewed.

The solution of many criminalistic problems depends upon comparison of material of unknown origin to material of known origin. Since there is no human control of trace-level constituents, the agreement of concentration levels for these constituents in two samples is strong evidence for their having a common origin. Chemical analysis or analysis by physical methods has been used frequently for comparison, but the greater sensitivity of the neutron activation technique makes it more attractive to the forensic scientist interested in the unique identification of material as an aid to criminal investigation. The usual intact preservation of test specimens, which keeps them available for presentation in court, is also advantageous.

Chemists trained in radioanalytical techniques can identify and quantitatively estimate elements present in a small sample of material by use of neutron activation analysis (NAA). The sensitivity of the technique enables the determination of about 70 chemical elements—some in amounts as small as 1×10^{-7} μg. In a strand of hair weighing only 0.3 mg, 12 to 14 trace elements can be determined. By ordinary chemical analysis, elements present in such small amounts are rarely detected or determined.

The radiochemist charged with the responsibility for analyzing a test material may not appreciate fully the function of the criminalist whose role it is to develop the results of the analysis into useful legal evidence. If the criminalist is to make profitable use of ability of the nuclear scientist to make comparative analyses, a useful working liason must be established. Mutual understanding of points of view has to be developed so that common and singular problems may be resolved.[1]

In the application of NAA to criminalistic problems, two fundamental problems exist: (1) the initial total lack of information as to any trace component that has not been previously detected by chemical means and (2) the maintenance of the integrity of both unknown samples and those taken for comparison. To provide a firm, statistically sound basis for establishing the validity of comparison, a great deal of information concerning the existence of trace elements in various materials must be acquired. The integrity of sampling is equally important; the number of samples required and the method of collection have to be established. These difficulties are demonstrated in the discussion of the specific uses of NAA.

By specific reference to selected original articles, the material presented in the following review covers the varied uses and aspects of NAA for forensic purposes. The chief use of NAA is in the unique identification of individuals and materials by comparison of trace-element content and the authentication of questioned objects by the same means. Examples include comparisons of hair, paints, soot, inks, gunpowder residues, glass and other automotive materials, drugs, paintings, and coins. The availability and costs of NAA services are also discussed.

Identification of Hair by NAA

Hair is a material frequently found at the scene of a crime. Especially in cases of rape, pubic and other body hair can be relevant to the identification of a suspect or, equally important, to negation of a suspect's guilt where superficial similarities[2] exist. The great potential value of hair identification and comparison led to the investigation of trace-element determination in hair by NAA.

The first workers on the problem of hair identification assumed that because a single hair could be activated and a gamma spectrum obtained, which is indicative of trace elements within the hair, a sufficient identification could be made with a hair taken from a suspect. The gamma spectrums of individual hairs (Fig. 1) show a similarity in many respects to

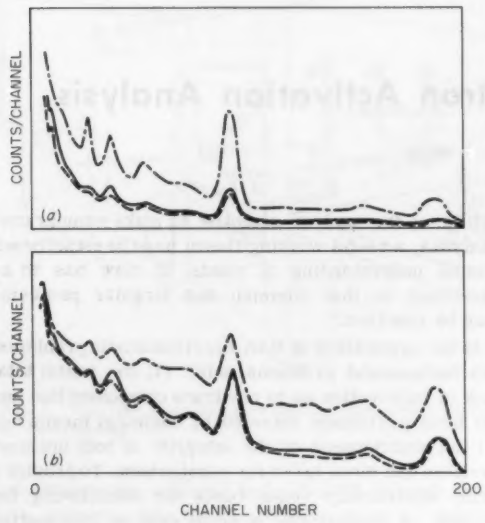


Fig. 1 Gamma-ray spectrums in linear and logarithmic display of irradiated hair (a) Gamma-ray spectrums comparing two head hairs from one person with a third head hair from another person (linear display). (b) Gamma-ray spectrums comparing two head hairs from one person with a third head hair from another person (logarithmic display).

the "pattern" evidence that is common in forensic work: fingerprints, bullet striations, absorption spectrums, chart tracings from a gas chromatograph, etc. The photopeaks and Compton edges that are evident in a 200- to 500-point gamma spectrum are identifying features, readily usable for comparison with similar material to assess identity of origin.[3,4]

More recently the General Atomic group[5] proposed the identification of hair by matching of weight-normalized spectrums plotted in both linear and logarithmic modes. The matching procedure as proposed, although an excellent first approximation to the problems, was inadequate. The report stated that, of 11 actual hair cases studied, only one yielded positive results, i.e., all spectrums for one hair were virtually identical to those of the other hair when these were obtained under the same conditions. In summing up their work, Bryan and Guinn[5] stated that, if meaningful results are to be obtained from the analysis of hair from actual cases, more work will have to be done to determine what limits of variation can be tolerated when making a decision as to whether or not two hairs are identical.

The validity of a simple comparison was soon disputed by other workers. Many factors, which were overlooked at first, came to light. The nature of hair itself, the different rates of growth for hair on the same head, the effect of time lapse on element concentration levels for hairs from the same head, the establishment of normal concentration levels in hair for the general population within an immediate area, and the effect of shampoos, medication, and environmental contaminants all must be taken into account. In addition, changes in instrumental conditions under which the gamma spectrum is recorded may also cause large differences in the gamma spectrums from the same test specimen.

According to Jervis[6] the comparison-of-spectrums technique was made more powerful by the use of photopeak ratios rather than the comparison of the intensities of the individual photopeaks. Using experimentally measured photopeak ratios is, in effect, the same as using an internal reference standard as a basis for normalizing all relative nuclide concentrations and minimizes variations in absolute concentration resulting from variable moisture content or dilution by innocuous foreign matter.

Jervis adduces the argument in favor of the comparison of peak-pair ratios—i.e., in the comparison of eight individual ratios, the probability of agreement to within 10% of those eight ratios (whose values may vary by more than 400%) would be very small if the samples were *not* identical. Conversely, there is evidence that similar samples are consistent in microcomposition to within a 10% or slightly higher agreement level. It thus appears that the probability of making a false comparison of samples not identical in origin as a result of the "chance" coincidence to approximately 10% in each of eight independent ratios is very small—of the order of 10^{-8} to 10^{-7} or less.

Lima, Shibata, and Atalla,[7] in Sao Paulo, Brazil, have also considered the problem of human-hair individualization. They used the same approach as Jervis—the comparison of peak ratios. They observed noteworthy changes in composition of pubic hair with increase in distal length.[7]

Where possible, Perkons and Jervis prefer[8] the strictly instrumental method, based on peak-pair comparison, over the radiochemical method of analysis on the grounds that radiochemical methods are more tedious and require greater skills, are time-consuming so that short-lived isotopes are lost by decay, and are destructive of physical evidence. Radiochemical methods provide, however, a feasible approach to the determination of trace elements in a matrix that is itself easily activated. More sophisticated counting equipment, now available, may eliminate previously necessary radiochemistry.

Bate and Dyer[9] also have been interested in the problem of identifying individuals by determining

trace elements in hair. In spite of their doubts about the simple spectrum analysis and the peak-pair comparison methods, these investigators concluded that the NAA technique showed promise if (1) a relatively large number of trace elements can be measured precisely, (2) all hairs can be ascribed to their respective donors and therefore the hair-to-hair variation is made small, and (3) the conditions of the sampling can be closely controlled to prevent contamination.

The importance of factors other than instrumental was also shown by further work by Bate and Dyer. Before trace elements within a hair can be determined, residues on the surface of the hair must be removed. Washing with a nonionic detergent, e.g., Kyro EO, is recommended.

A most important observation made by Bate and Dyer is that the trace-element composition of hair is altered by environmental adsorption. The observation is based on the following experimental facts:

1. Hair composition is altered drastically by application of certain dyes and medicinal agents.
2. The concentration of most elements increases with distance from the scalp toward the outer ends.
3. Radioiodine given to thyroid patients is soon found strongly adsorbed in the outer ends of the patients' hair. Since this could not have been incorporated into the growing hair, the iodine must have been adsorbed from perspiration.
4. When hair samples are placed in an aqueous solution that contains ions of various elements and are then removed and washed, these elements will still be adsorbed on the hair in amounts greater than those in untreated control hair samples.

Possibly because of the adsorption of trace elements from environmental sources, or because of differing growth phases of individual hairs, Bate and Dyer found such a large variation in hairs from the same head as to make the matching of single hairs questionable. The analysis of only one hair is probably not sufficient to enable the matching of the hair to an individual donor. Work presently in progress may change this outlook.

The adsorption on and elution of trace elements from human hair were studied by Bate[10] as phenomenons related to the contamination of hair samples. The amounts of the elements adsorbed from synthetic perspiration solutions depended on the *p*H of the solution and the particular element used (Table 1). Sodium, potassium, and cesium were not adsorbed. Table 1 lists ions adsorbed from a synthetic perspiration solution at three different *p*H values. Figure 2 shows the adsorption and removal of manganese, copper, and zinc ions from hair. The conclusion important to forensic application is that the concentration of almost any trace element in hair could easily be changed by addition of a neutral solution of the metal ion to the hair. Contrary to Kirk's[1] assertion that there is no human control of trace constituents, Bate's work indicates that these can be changed at will.

Although the results of a study on animal hair cannot be extrapolated to human hair with any surety, Kennington's[11] work on antelope hair is pertinent to the question of trace-element removal. His study on the removal of sodium from antelope hair showed that a part of the sodium present could be removed by extended washing with water, but that approximately 40% of the original amount was retained. Bromine and nickel were completely removed by washing, while manganese, copper, and zinc were not; this indicates that, among other factors, ionic radius and charge may be involved in the control of distribution of trace elements in hair.

In assessing the results of their study of trace elements in hair and possible identification of persons by hair matching, Bate and Dyer[9] reject a simple comparison of gamma-ray spectrums and would require the identification and quantitative measurement of the trace elements. The use of photopeak ratios is also considered inadequate since the ratios are not unique quantities. These authors recommend that criminal investigators not attempt comparison of single hairs found at the scene of a crime; instead, the art of identification should be advanced by carrying out simulated cases until enough data have been accu-

Table 1 CONCENTRATION OF ELEMENT ADSORBED ON HAIR FROM SYNTHETIC PERSPIRATION SOLUTION

Element	Element concentration, μg/g hair		
	*p*H 3.5	*p*H 4.5	*p*H 5.5
Au^{3+}	28,000	27,300	26,200
Hg^{2+}	3,300	5,100	6,600
Zn^{2+}	131	440	920
Ag^{+}	420	520	640
Cu^{2+}	28	102	255
Fe^{3+}	21	40	120
Cr^{3+}	26	61	96
Co^{2+}	3.8	20	95
Cr^{6+}	15	41	88
Mn^{4+}	3.3	13.5	69
Se^{4+}	215	116	47
Cl^{-}	400	132	35
Ba^{2+}	2.1	8.0	25
Br^{-}	158	66	20
I^{-}	85	31	10
Sr^{2+}	0.72	2.7	9.8
Ca^{2+}	0.37	1.5	8.0
Sb^{5+}	8.8	4.5	2.7
P (as PO_4^{3-})	6.1	2.0	1.66
As^{3+}	0.51	0.58	0.76
As^{5+}	4.2	1.7	0.66
Na^{+}	0	0	0
K^{+}	0	0	0
Cs^{+}	0	0	0

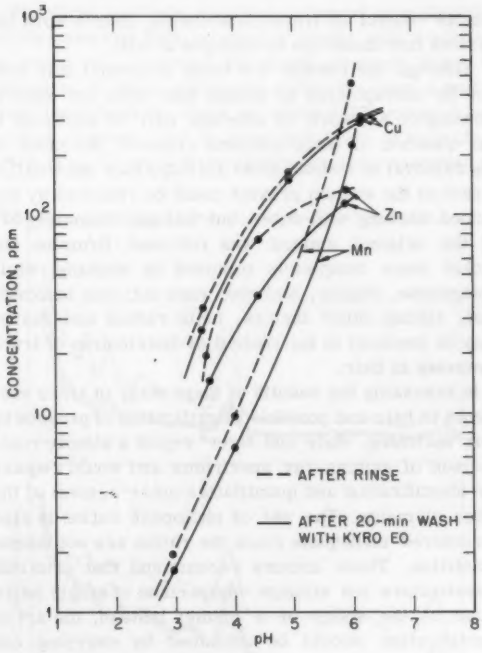


Fig. 2 Adsorption by hair of manganese, copper, and zinc from simulated perspiration and effects of Kyro EO washing after adsorption. ——, quantity found after rinse; — —, quantity found after 20-min wash with Kyro EO.

mulated to attest to the validity of identification by hair comparison.

Some of the most promising work is that of Coleman,[12] who based his investigation on a statistical model developed by J. B. Parker.[13] Parker's article on the statistical treatment of identification problems is a thorough and detailed discussion that should be consulted for a complete consideration of the matter. In relating the composition of hairs taken from a suspect's head to those found at the scene of a crime, he takes into account not only the analytical errors attendant on establishing, for example, the sodium content of the hair but also a "natural" variation, referred to as *intrinsic variation*, due to the physical differences in composition from one hair to another on a suspect's head. The general problem is stated thus: a number of different attributes—each capable of measurement, each subject to measurement error and possibly, as in the case of hair, intrinsic variations as well—are available for comparison. How are we to assess, numerically and unambiguously, the evidence that these several comparisons provide?

Many factors determine the assistance that a given attribute, capable of numerical measurement, may provide in identification problems. If the magnitude of the experimental error of actual measurements can be reduced, the attribute is of greater value for providing useful evidence toward identification. The intrinsic variation, such as in the chemical composition of hairs taken from different places on a person's head, may be so large that this particular attribute is of little value in identification. The most important factor is the degree of variation that occurs in the attribute from one individual to another. For example, even if the sodium concentration in a single hair could be measured very accurately and even if the concentration over the head of any individual varied little, the attribute would still be valueless for identification purposes if everyone had hair of similar sodium concentration. An index is required that would measure the efficiency of an attribute by relating the ratio of the measurement errors to the variation in the population.

Parker has developed such a useful index from statistical consideration. He concluded that attributes that can be measured numerically may be used as an aid to the identification problem by computing, for each attribute, the reduced deviation, E, defined by

$$E = (\chi_i - \xi_i)/\sqrt{\sigma_i^2 + \theta_i^2} \qquad (1)$$

where χ_i and σ_i are the measured values and the standard deviation of the ith attribute found at the scene of the crime, respectively, and ξ_i and θ_i, those of the suspect brought in for questioning. A "discrepancy" index, C, can be formed by adding the sum of the square of the E's. This may now be compared with a certain critical value, C_0, that is tabulated in a standard table, and if C exceeds C_0, the suspect may be released from suspicion.

Coleman[12] tested Parker's thesis by studying hair identification in Great Britain. For use of Parker's method of data analysis, a knowledge was required of (1) the frequency distribution of mean values of trace-element concentrations for the general population and (2) the measured variation in trace-level concentrations among hairs from a single head, including the intrinsic or "natural" variation and the experimental error of the measurements.

To obtain a satisfactory representative sample of hair from the general population for analysis, a survey letter requesting a sample of hair and the return of a questionnaire was sent to 1200 people chosen randomly from the electoral registers of England and Wales. A satisfactory return was obtained from 70% of the selected group. All the returned hair samples were analyzed for Na, Cl, Mn, Br, I, Cu, Au, Hg, Cr, Zn, Sb, and Ca. In some cases Se, Ag, and Ba were also determined.

Interesting results emerged from the study. The distribution curves for all elements measured were significantly different for males and females. The previous assumption that the variation over a single head was approximately the same as for all heads was shown to be invalid; consequently, for legal evidence, the variation in trace-element concentration among

hairs on each suspect's head must now be established. A definite variation in trace-element concentrations with time was established by a concomitant study. The comparison of values among hairs taken over a period of time from the same head showed values differing so much that, beyond a period of 70 days, a comparison was useless. Thus a library of hair analyses of known criminals would be worthless in crime detection. Other results noted were (1) the variation in trace-element concentration caused by hair treatment, e.g., bromide and iodide from shampoos and neutralizers, (2) high concentrations of certain elements because of occupational environments, and (3) correlation of calcium content with water hardness of the area.

Parker's expression, Eq. 1, shows that the value of the evidence obtained from hair analysis is inversely proportional to the standard deviation of concentrations over a single head. Any reduction in variation is thus of value, and every effort was made by Coleman to reduce experimental error. A standardized procedure for washing each hair with diethyl ether and irradiating each hair twice in the Herald reactor in a flux of 4×10^{12} n/(cm^2)(sec) was developed. The samples were counted in a gamma spectrometer, without previous radiochemical separation; the complex spectrums were resolved by a machine-computed least-squares analysis. Values obtained in replicate analyses of hair samples are shown in Table 2.

In a simulated test involving 10 samples of hairs from 10 individuals (criterion C was set to include 99% of the hairs as sampled from each suspect's head), correct matching was achieved in 9 of the cases.

The results of Coleman's work cannot be safely extrapolated to other regions of the world because of the effect of locale on trace-element concentrations in hair. Bate and Dyer,[14] in a comparative study of the concentration of 12 elements in hair among groups of people in Oak Ridge, Tenn.; Hastings, New Zealand; and Napier, New Zealand, found significant differences (Table 3) clearly demonstrating that norms must be established for the general population and for single heads for each area until the extent of general applicability has been determined.

Table 2 REPLICATE ANALYSES ON HAIR SAMPLE

Sample No.	Natural logarithms of concentration, ppm						
	Cl	Na	Cu	I	Mn	Br	Ca
1	6.425	4.434	2.907	1.740	−1.171	1.902	7.485
2	6.612	4.615	3.035	1.840	−1.078	2.015	7.621
3	6.668	4.727	3.174	1.775	−1.050	1.988	7.678
4	6.494	4.577	2.965	1.482	−1.273	1.872	7.529
5	6.801	4.836	3.231	1.917	−0.968	2.092	7.529
6	6.750	4.754	3.059	1.856	−1.107	2.163	7.415
7	6.797	4.836	3.250	1.629	−0.968	2.092	7.912
Mean	6.650	4.685	3.089	1.748	−1.088	2.018	7.595
Standard deviation	0.148	0.148	0.140	0.149	0.110	0.106	0.164
Contribution to total activity, %	73.8	17.8	1.1	0.3	1.3	1.1	4.6

The conclusions drawn from Bate and Dyer's work are of interest from the viewpoint of minimizing errors in comparing hairs from the same head. They suggest that (1) hair be thoroughly cleaned from surface contamination; (2) sodium, bromine, and chlorine not be used in matching hair samples because of the probability of rapid fluctuation in content of these elements in hair; (3) those elements which are most tightly bound to the hair fiber be used for forensic analysis; (4) environmental adsorption is probably a major source of trace elements found in hair; (5) samples for comparison should be of equal lengths and distances from the scalp since trace-element concentrations in hair vary greatly with distance from the scalp; (6) concentrations of trace elements in hair are essentially uncorrelated; and (7) people of diverse backgrounds are more likely to have greater variations in trace-element concentrations than people of similar backgrounds.

From the above discussion the divergence of opinion among investigators as to what constitutes a legally

Table 3 MEANS, RANGES, AND DEVIATIONS OF TRACE ELEMENT CONCENTRATIONS IN HAIR

Element	Origin of Samples								
	Oak Ridge, Tenn.			Hastings, New Zealand			Napier, New Zealand		
	Concentration, ppm			Concentration, ppm			Concentration, ppm		
	Mean	Range	R.S.D.,* %	Mean	Range	R.S.D.,* %	Mean	Range	R.S.D.,* %
Zn	177	51–602	73	126	101–186	14	132	85–166	15
Cu	34.1	7.8–234	87	30	7–93	103	15.5	8–150	97
Hg	7.6	0.1–33	140	2.2	0.3–34	59	1.8	0.5–5.3	49
Mn	2.1	0.08–22	293	1.0	0.9–2.6	91	1.0	0.2–4.4	90
Au	4.3×10^{-2}	$(0.08–27) \times 10^{-2}$	137	2.9×10^{-3}	$(0.8–19.7) \times 10^{-3}$	86	2.7×10^{-3}	$(0.8–12) \times 10^{-3}$	59
Ag	3.8	0–12	93						
As				2.4	0.4–7.9	54	1.8	0.7–5.3	108
Sb	1.5	0.5–4	500	0.69	0.1–1.4	116	0.36	0–4.4	86
Se	6.4	1–11	92	0.53	0.4–12.2	25	0.69	0.4–0.9	29
Al	4.4	2–9	109	3.4	1.6–7.8	59	4.9	1.2–9.2	40
Mo				6.4×10^{-2}	$(1.9–12) \times 10^{-2}$	41	6.3×10^{-2}	$(0.4–13.0) \times 10^{-2}$	33
W				1.9×10^{-2}	$(0.3–4.2) \times 10^{-2}$	89	1.3×10^{-2}	$(0.4–6.4) \times 10^{-2}$	76

*R.S.D., % = standard deviation × 100/mean.

acceptable hair comparison and identification is obvious. Claims made by one worker are viewed with skepticism by another. The true worth of the method can be evaluated only by a continuing dialog between experienced investigators. If the evidence based on NAA is introduced into court, the dialog will be voiced by legal counsel on the basis of their knowledge of the literature. In the interests of justice, the full merits of NAA data as evidence should be openly discussed and widely publicized.

Some of the difficulties that cause the divergence of opinion are immediately apparent and require consideration. The factor that makes hair identification possible also operates as a possible disadvantage: the tremendous sensitivity of NAA—its ability to detect quantitatively very small amounts of trace elements in hair—makes it also vulnerable to error because of chance contamination. A major problem is the decision as to what is an intrinsic component of the test specimen and what is extraneous contamination. The smallness of sample permitted because of the sensitivity of the NAA technique may cause the investigator to overlook the problem of inhomogeneity that is ever present in dealing with solid materials. Training of the chemist not only in the performance of the analysis but in all the fundamentals of microchemistry is essential so that the laboratory environment does not contribute to the sample's constituents. Indoctrination of criminal investigators into proper sampling techniques is also required; sampling should be done in accordance with established statistical procedures so that norms and deviations from a norm can be based on objective rather than subjective criterions. Identification and quantitative determination of the elements are necessary. If the above requirements are met, hair identification by NAA may advance to a legitimate place among criminalistic tools; without soundly based and rigorously carried-out experimentation, it will remain a scientific bugaboo used to frighten the uninformed.

NAA of Hair in the Detection of Poisoning

Jervis et al.[3] make the point (to be noted especially by persons not adept in chemistry) that, although neutron activation analysis can readily be applied to the determination of trace elements in hair, it cannot be used to detect toxic organic compounds such as strychnine, barbiturates, histamines, morphines, and related narcotics. NAA is useful only for elemental analysis; however, normal and toxic levels of elements in hair can be established. The element most widely known and readily available as a poison is arsenic. Because arsenic is a poison easily detectable by the sensitive techniques of NAA, many workers have studied its occurrence in hair. Here again much disagreement is noted as to what are normal levels and what constitutes an abnormally high level indicative of poisoning.

Lima, Shibata, and Atalla[7] studied arsenic in hair in connection with hair identification. They found that hairs of workers in an arsenic plant showed a level much higher than the 5 ppm that they considered normal. The investigation clearly showed that continuous exposure of the subject to dust, fumes, etc., may give a high concentration of the environmental elements in hair. An interesting observation, perhaps confirming the legend of King Mithridates VI, is that the workers in the plant may have acquired immunity from arsenic poisoning by the administration of gradually increasing doses of arsenic.

G. B. Baro et al.,[15] working in Buenos Aires, determined the arsenic content of human hair by irradiation of hair samples in the RA-1 reactor (Reactor Argentino de Irradiacionas modified and redesignated as RA-1). Arsenic-76 was separated radiochemically from other nuclides and determined. According to Baro, 1.0 ppm was found in samples from normal subjects while an average of 2.2 ppm was found in samples from a victim of arsenic poisoning. The coefficient of variation was 10 to 15%.

In 1964 Smith[16] discussed the question of the interpretation of the arsenic content of human hair. According to him the median concentration of arsenic in 1000 human-hair samples as determined by NAA is 0.51 ppm. For males the median is 0.62, but for females, only 0.37 ppm. Levels greater than 2 to 3 ppm are indicative of poisoning; however, external contamination may also produce a high value. Similar linear sections of hair of several millimeters length over the region of interest were analyzed to permit proper evaluation. These sections were not washed prior to analysis. Studies of arsenic excretion indicate that levels in hair drop to normal within 3 weeks after a single oral ingestion.

The apparent ease of the determination of arsenic in hair has led to the analysis of the hair of deceased historical personages whose deaths may have been caused by arsenic poisoning. Smith, Forschufvud, and Wassen[17,18] examined hair taken from the head of Napoleon at various times[17] before and after his death. Analyses indicated that Napoleon was intermittently exposed to arsenic over a period of 4 months, but the evidence does not appear to offer conclusive proof that Napoleon's death was caused by arsenic poisoning. Christell and Sjostrand[19] analyzed the remains of King Erik XIV of Sweden by activation analysis techniques in an attempt to verify the theory that he died from arsenic poisoning. Here again the experimental evidence does not justify an unqualified statement as to the cause of his death.

Erikson,[20] who recommends the radiochemical procedure for the estimation of arsenic in hair, has further attempted to relate arsenic content to criminal poisoning. In this connection he relies upon the analyses carried out by Smith[16] to state that, if the arsenic content of hair sections is greater than 3 ppm,

the individual has been exposed to arsenic. In a number of cases, evidence of arsenic poisoning obtained by neutron activation analysis has been introduced into Canadian courts.

A possible spin-off benefit, aside from criminalistics, is the establishment of norms for trace elements in human hair. The importance of trace elements to the normal functioning of animals, including humans, has been well established by the pioneer work of Comar[21] and others, as reported by Underwood. The difficulty of representative sampling of animals and humans is obvious. If norms could be established for trace-element levels in human hair, then the possibility exists of correlating deviations from the norm with clinically observed signs. The sampling for NAA would be the simple and easy collection of hairs from a number of sites on the head.

The Identification of Miscellaneous Materials

The cases in which American courts have accepted NAA as evidence (see Appendix A) indicate that the technique has been much more successfully used for identification of other materials than for hair. Paint, soot, soils, inks, gunpowder residues, glass, and "moonshine" whiskey have all been subjected to comparative analysis by NAA.

PAINT

Paint is an item which frequently forms an essential link in criminal cases, and it is an ideal material for NAA since it is subject to close manufacturer's control and is usually of uniform composition. Typical gamma-ray spectrums obtained in the course of an investigation are shown in Fig. 3. Bate et al.[22] have

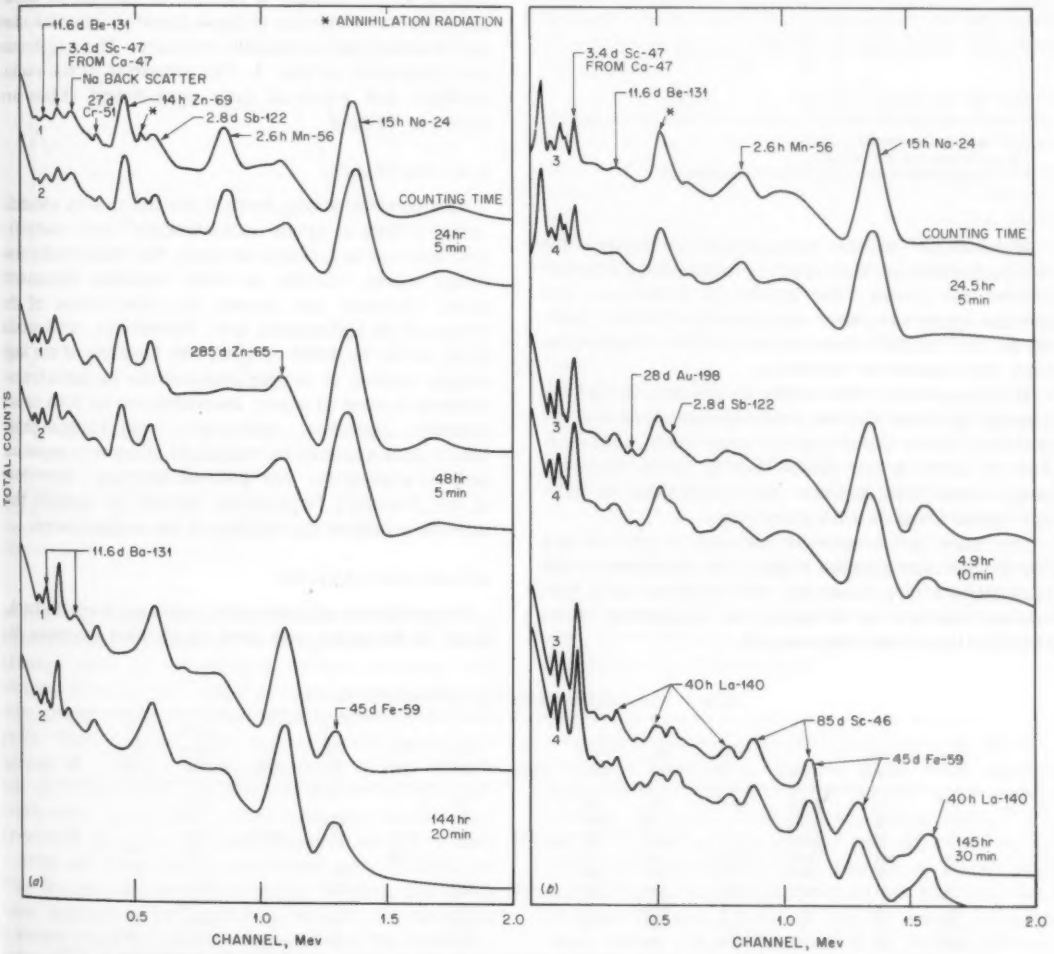


Fig. 3 Paint from boards in illicit whiskey investigation. Irradiation time, 1 Mw for 40 min; flux, 2×10^{12} n/(cm²)(sec); decay time, as shown, crystal, 3- by 3-in. NaI(Tl); counting time, as shown; energy range, 0 to 2 Mev; specimen (a) 11 cm from crystal, (b) 5 cm from crystal.

studied paint identification and tabulated (Table 4) the elements typical of black automobile finishes.

Bryan[23] has also pointed out that paint is important as physical evidence because it is such a common material, easily transferable from one object to another. He has under way a large-scale survey analysis of many paints of different colors and types. Paints from different manufacturers have already been found to be quite different, qualitatively as well as quantitatively. Both Bate[22] and Bryan[23] have demonstrated the ability to compare paints for identification. Of value in this connection is the ability to preserve the comparison sample for presentation in court, since neutron activation does not destroy the evidence.

Table 4 ELEMENTS FOUND IN AUTOMOBILE PAINT FINISHES

Paint	Mn	Ba	Zn	Co	Na	Cu	Cr	P	$^{139}Ba/^{56}Mn$	$^{131}Ba/^{65}Zn$
1	P*	P	P	P	P		P		2	1.5
2	P	P	P	X†	P	X			4	5
3	P	P	P	D‡	P	X			10	5
4					P	P		P		
5	P			P	P					
6	P	P	P	D	P	X			10	5

*P = definitely present.
†X = possible but not definite.
‡D = detected as present but at limit of detection.

Wyttenbach[24] at the Eidgenossisches Institut fur Reaktorforschung, Wurenlingen, Switzerland, also examined car paints. The paints on American- and German-made cars were significantly different (Table 5). He also concluded that paints could be identified by NAA with reasonable certainty.

In a report for 1964–1965, Bryan and Guinn[5] recounted the details of the first time that NAA was introduced into a California (or any) state court—on July 3, 1964, in San Mateo County, Calif. The case hinged upon identification and comparison of paint specimens found on a burglary tool.

The case is of interest not only because it is a "first" but also because it made use of statistics and probabilities to present the NAA evidence in a systematic way so as to assure the acceptance of the identification of the paint sample.

SOOT

Bate et al.[22] use the analysis of soot particles to illustrate one of the pitfalls in the use of NAA. Because the method is so very sensitive, there is a tendency to use very small test specimens. If the sample is not minutely homogeneous, erroneous and misleading results may be obtained. Two apparently identical portions of soot samples indicated in one case an inhomogeneous distribution of elements in the sample that prevented identification.

SOILS

Soil samples have also been analyzed by NAA,[22] and techniques involving different radiation exposure times have been worked out which will permit the satisfactory comparison of soil samples. The technique has been put to good use in the identification of soil samples from the vicinity of illicit still operations showing soils to be similar to those found on vehicles used for transporting moonshine whiskey. The spectrums are compared in Fig. 4. The identities of the radionuclides and some of their peak-height ratios are shown in Table 6.

INKS AND PRINTS

The nondestructive method for the in situ identification of inks or prints on documents[22] is of considerable interest in forensic science. The owners of questioned bonds, checks, or other valuable documents would certainly not permit the destruction of the papers in an authenticity test. Potentially, NAA would seem to be an ideal method, but, because of the high sodium content of writing inks and the variable trace-element content of paper, identification by NAA is not possible. However, typewriter- and carbon-paper prints may possibly be compared at least to point out lack of similarity. The Internal Revenue Laboratory of the Treasury Department intends to continue this work to establish the validity of the comparisons.

GUNPOWDER RESIDUES

The detection of gunpowder residues from the backblast of firearms may also be of value in crime de-

Table 5 ELEMENTS PRESENT IN AUTOMOBILE PAINTS

Test No.	Auto make*	Year	Ba, %	Na, ppm	Mn, ppm	Cl, ppm	Sb, ppm	Cu, ppm	Zn, %	Sr, ppm	Arbitrary units	Co, %	Sc
10	X	1953	0.52	220	50	†	35				35		
11	X	1954		160	140		361		42				
12	X	1957	7.6	1310	180	1050		15	21	1560	28		N
14	X	1960	25.8	35	40			14			4	N†	
17	X	1961	9.6	1340	230				22			N	N
16	Y	1963	10.6	190	57	185	117		22		210		
21	Z	?	18.6	131	35		62		11		7.6		
22	Z	?	3.0	267	178		610		0.7		500	35	
23	Z	?	12.4	36			150		4		58	9.6	

*X and Y are two large German automobiles; Z is an American make.
†Data details: an empty space denotes that the element was not detected; an "N," that is was not quantitatively determined.

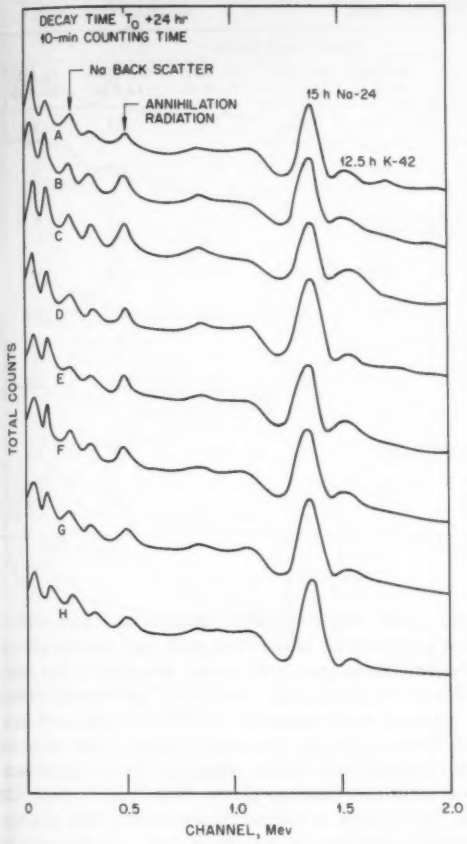


Fig. 4 Gamma-ray spectrums of soils in illicit whiskey investigation. Spectrums A and B taken from truck soil specimens; spectrums C to H taken from soils at suspect's residence; irradiation time, 1 Mw for 10 min; flux, 2×10^{12} n/(cm²)(sec); decay time, as shown; crystal, 3- by 3-in. NaI(Tl); counting time, as shown; energy range, 0 to 2 Mev; specimen, 10 cm from crystal.

tection. The chemical method that uses the reaction of diphenylamine with nitrate is unreliable. Since most primers used in ammunition contain antimony and barium, Ruch et al.[25] have studied the possibility of determining these elements from hand swabs of suspects. Their results indicate that levels higher than normal by a factor of approximately 40 for barium and 10 for antimony are found on hands that have recently fired guns. Rather than using the paraffin cast previously used for the diphenylamine test, they used a swipe of filter paper moistened with 1% HNO_3 to wipe the skin surface. According to Ruch the technique appears to be promising, not only for detecting a recent firing but also for ascertaining the manufacturer of the ammunition used, the number of times the weapon was fired, and, from the distribution of the residue on the hand, the type of weapon fired.

In more recent work Guinn[26] reported the return to the paraffin-cast method of removing gunshot residues. The recommended procedure calls for coating the thumb-web area of the hand with a liquid layer of the purified paraffin, removing the paraffin after solidification, breaking the paraffin up and placing it in small polyethylene vials, activating it with thermal neutrons, dissolving all but the paraffin, radiochemically separating any induced 84-min ^{139}Ba and 2.8-day ^{122}Sb present with barium and antimony carriers, and counting the recovered nuclides. Three ORNL chemists — F. F. Dyer, L. C. Bate, and J. F. Emery — are shown in Fig. 5 studying the proper method of applying the paraffin cast. General Atomic has made a special gunshot-residue kit available to law-enforcement agencies which simplifies the taking of proper samples. Guinn reports that the method yielded positive results when tested on suicide victims. In three murder cases positive results were obtained, and in each case the suspect later confessed the murder.

In related work, S. S. Krishnan[27] studied the determination of the distance of the fired gun from the victim. The establishment of the distance can preclude the claim of suicide or struggle. Krishnan chose to establish the distance by NAA for traces of antimony and copper rather than the more conventional tests for gunpowder. His procedure required the firing of test shots on target material of filter paper or clothing, removal of sections of target material at various distances around the bullet holes, neutron activation, and radiochemical separation of ^{122}Sb and ^{64}Cu by ion exchange. Antimony and copper patterns can be seen within acceptable limits up to a distance of 10 ft or more. Evidence of gunshot distance as determined by NAA was introduced in the inquest into the death of Susan Marie Black at Fort William, Ontario, Canada.[27]

Doubt can arise during criminal investigation as to whether a hole was in fact caused by a bullet.[27] The analysis of swabbings from around the bullet hole by NAA for traces of antimony and copper can substantiate the assumption that a hole in leather, paper, or cloth was indeed made by a bullet. In favorable cases even the caliber of the weapon from which the bullet was fired can be determined.[28]

GLASS

Because glass — a frangible material — is often involved as evidence in criminal cases, it too has been investigated to see if various batches can be differentiated by trace-element composition. Settle[29] reported that some longer-lived activities can be detected if sufficient time is allowed to elapse after irradiation so that sodium activity has died out. Some of these elements are Sc, Hf, Ba, Zr, and Sb; probably other metals can also be detected by varying the conditions of the analysis.

Jervis[6] was also interested in the comparison of glass samples obtained from automobile manufac-

Table 6 RADIONUCLIDES FOUND IN SOIL

Radionuclides	$T_{1/2}$	Gamma radiation, Mev	Samples	Peak-Height Ratios						
				Na 1.37/ K 1.52	Na 1.37/ La 0.32	Sc 0.89/ Fe 1.29	Np 0.11/ Cr 0.32	Cr 0.32/ Au 0.41	Ce 0.145/ La 0.49	Ba 0.22/ Sc 0.89
^{131}Ba	11.6 days	0.12, 0.22, 0.27, others	A	4.7	0.7	3.4	2.4	1.6	2.1	0.9
^{141}Ce	32 days	0.145	B	4.6	0.6	3.5	2.2	1.7	2.3	0.9
^{51}Cr	27 days	0.32								
^{198}Au	2.8 days	0.41	C	4.8	0.7	3.4	2.2	1.6	2.0	0.8
^{59}Fe	45 days	1.09, 1.29,								
^{140}La	40 hr	0.32, 0.49, 1.59, others	D	4.9	0.7	3.4	2.3	1.8	2.4	0.8
^{56}Mn	2.6 hr	0.85, 1.82	E	5.0	0.7	3.2	2.5	1.8	2.5	0.9
^{239}Np*	2.39 days	0.11, 0.22, 0.28								
^{185}Os	93 days	0.65, 0.75, 0.87	F	4.7	0.7	3.1	2.5	1.7	2.2	0.9
^{42}K	12.5 hr	1.52								
^{46}Sc	85 days	0.89, 1.11	G	4.6	0.7	3.2	2.2	1.8	2.1	0.9
^{47}Sc†	3.4 days	0.16								
^{24}Na	15 hr	1.37, 2.25, 2.76	H	4.5	0.6	3.1	2.2	1.6	2.6	0.8

*^{239}Np from ^{239}U. †^{47}Sc from ^{47}Ca.

turers. He suggested that, by use of peak-pair ratios, glass samples could be identified as being similar. Coleman, Wood, and Wood[30] in England have reported a continuing study of glass identification. Although they have made no definite statement as to results, their parallel analyses by NAA and spectroscopy are expected to be of value.

Fig. 5 Study of proper method of applying paraffin cast: left to right, F. F. Dyer, L. C. Bate, and J. F. Emery.

MISCELLANEOUS AUTOMOTIVE MATERIALS

Many other materials[25]—e.g., automobile-tire rubber, grease, plastic from taillights—have been examined by NAA in much the same manner as automobile glasses. Continuing efforts are being made to establish valid comparisons.

PHYSICAL EVIDENCE FROM ILLICIT STILL OPERATION

A problem of interest to the Internal Revenue Service is the comparison of physical evidence obtained from illicit still operation.[4] Moonshine whiskeys have been analyzed for trace elements, and significant differences were obtained among samples from seven different sources (Fig. 6). Table 7 shows the results of element determination by NAA of eight soil samples from a typical law-enforcement case involving transportation of illegal whiskey. Similarity of samples from the vicinity of the defendant's home with soil taken from a trailer truck loaded with non-tax-paid spirits seized in New York City was satisfactory enough to be accepted by the judge, defense counsel, and jury in a federal court. Paint samples related to illicit still operations were also compared satisfactorily by NAA.

Identification and Tracing of Drugs

PHENOBARBITAL AND PETHIDINE HYDROCHLORIDE

Legally manufactured drugs that have passed into illegal channels pose a serious problem for law-enforcement officers. The ability to trace these drugs back to their points of origin can be important. Other chemical and physical methods of analysis have failed because of lack of either sensitivity or selectivity to provide positive identification between unknowns and samples of known origin. Bate and Pro[31] have applied NAA to this problem because it has the twin virtues of extreme sensitivity and adaptability to nondestructive measurement. Phenobarbital and pethidine hydrochloride were the test drugs in the study. Bate and Pro concluded that activation analysis, combined with gamma spectrometry, is a feasible technique for the identification of certain trace elements in drugs and

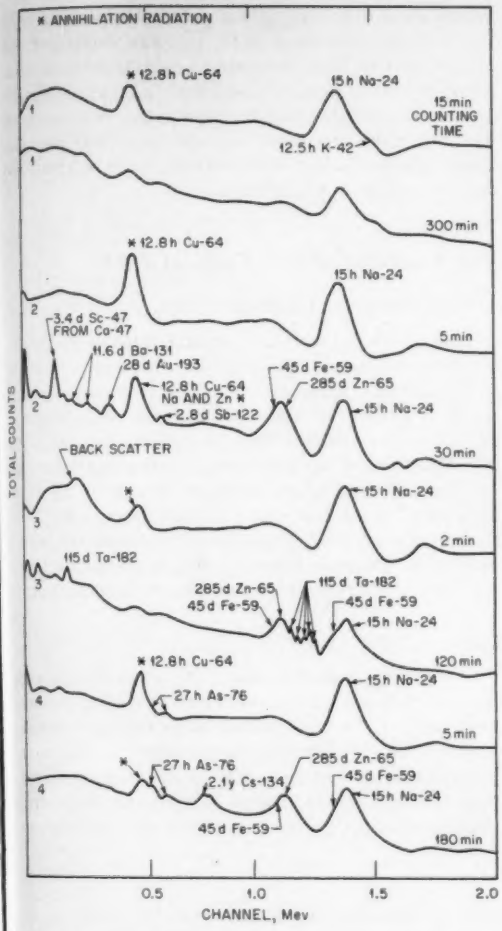
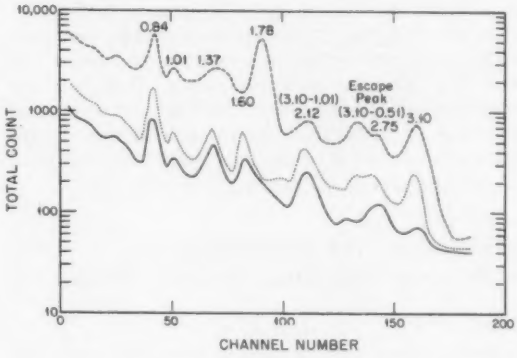


Fig. 6 Gamma-ray spectrums of moonshine whiskeys. Irradiation time, 10 Mw for 1 min; flux, 2×10^{12} n/(cm²)(sec); ----, decay time $T_0 + 3$ days; ——, decay time $T_0 + 10$ days; crystal, 3- by 3-in. NaI(Tl); counting time, as shown; energy range, 0 to 2 Mev; specimen, on crystal.

can be a potentially valuable tool in combating illegal traffic in drugs. Figure 7 shows the gamma spectrum of a barbital drug.

HEROIN

Work on possible methods of tracing heroin is still being carried on by Pro, Schlesinger, and Hoffman[32] at the Internal Revenue Service laboratories because of the importance of controlling traffic in drugs. Heroin, manufactured legally, could be tagged at the point of origin to permit easy NAA identification as an aid to tracing shipments found in illegal possession.



Radionuclide	Energy, Mev
^{49}Ca	3.10
^{24}Na	2.75, 1.38
^{38}Cl	2.12, 1.60
^{28}Al	1.78
^{27}Mg	1.01, 0.83
^{56}Mn	0.84, 1.81

Fig. 7 Gamma spectrum of a barbital drug. Irradiation time, 10 min; flux, 8×10^{11} n/(cm²)(sec), counting time, 1 min; geometry, 7.5 cm; absorber, 1/2 in. polyethylene, energy scale, 20 kev/channel; ----, decay time $T_0 + 10$ min; ...., decay time $T_0 + 20$ min; ——, decay time $T_0 + 30$ min.

Table 7 COMPARISON OF "MOONSHINES" BY NEUTRON ACTIVATION ANALYSIS AND GAS CHROMATOGRAPHY

Case No.	Sample No.	Elements, ppm										Organic congeners, g/100 liters				
		Na	Cu	Zn	Sr	Fe	Sb	Se	Au	Cr	Ce	Mn	Ethyl acetate	Acetaldehyde	*N*-propyl alcohol	Iso-butyl alcohol	Iso-amyl alcohol
107	1421	2.2	10.7	0.12	1.8×10^{-3}	T	T	*	*	*	*	6.3	3.8	28.0	5	18.5	72.5
	1422	3.0	11.7	0.13	2.0×10^{-3}	T	T	*	*	*	*	6.2	3.9	29.5	5	15.8	76.4
202	1472	1.0	15.6	T	*	*	*	3.0	T	*	*	10.2	28.0	47.5	4	18.8	56.4
	1473	1.1	15.8	T	*	*	*	3.2	T	*	*	10.3	27.0	47.2	4	19.5	56.8
	1474	1.1	16.0	T	*	*	*	3.8	T	*	*	10.2	27.5	47.0	4	19.2	57.0
	1475	1.1	15.7	T	*	*	*	3.2	T	*	*	10.1	28.2	47.5	4	19.7	56.9
342	985	4.0	0.07	1.3	*	*	*	*	*	0.32	0.90	1.4	0.9	5.2	5	15.8	39.2
	986	4.1	0.07	1.4	*	*	*	*	*	0.35	0.95	1.5	0.9	5.2	5	16.2	39.7
	987	4.1	0.08	1.3	*	*	*	*	*	0.31	0.90	1.6	0.9	5.3	5	16.2	39.8
	988	4.3	0.07	1.3	*	*	*	*	*	0.33	0.85	1.8	0.9	5.4	5	15.9	39.4
		By neutron activation analysis											By gas chromatography				

*Not detected. †T = trace, not calculable.

OPIUM

The analysis of opium and its derivatives by NAA has been considered as a means of tracing the origin of the drug. Workers[33] at Oak Ridge National Laboratory were able to analyze the samples for trace elements and to use codes for machine computing that enabled the quantitative estimation of elements from the recorded gamma spectrum. Unfortunately the analysis of the samples does not resolve the problem of tracing the drug's origin, since local variations in soils, fertilizers, and available moisture contribute uncertainties of such magnitude that positive assertions concerning origin cannot be made.

The Norwegian investigators Pappas, Alstad, and Lunde,[34] at the University of Oslo, also considered the identification of the origin of opium by NAA trace-element analysis. They determined gold and rare earths in opium by NAA and found 0.5 to 10 ppm gold and 20 to 150 ppm total rare earths. These workers concluded that their approach was promising and that their way of comparing samples could be used for the determination of the origin of opium. Their conclusion is not sustained by the Oak Ridge investigators.

Examination and Authentication of Paintings and Other Valuable Objects

WORKS OF ART

Works of art have become of interest recently not only because of their intrinsic artistic merit but also because of their potential value as investments and hedges against inflation. The critical examination of paintings by NAA[35] together with autoradiography may be used to reveal hidden internal structure of paintings, details no longer visible in faded areas, overlaid areas in which details of underpainting are covered by the final surface, and basic composition and distribution of materials within the object. By use of different conditions, the technique can reveal the locations on the painting of pigments containing different metals. Such autographs extend the information available from X-ray radiography that primarily shows the location of lead pigments. Faded photographic prints can be reproduced by similar techniques, and old manuscripts possibly can be regenerated.

STAMPS

Another interesting problem involves the comparison of postage stamps[32] claimed to have been misprinted and thus to be of extraordinary value. In one case, for example, activation analysis of small portions of the blue and orange areas from a control and a questioned stamp revealed that the questioned stamp had been chemically altered.

COINS

The authentication of questioned objects can sometimes be made by NAA. Pro et al.[32] have reported the verification of a 1943 *copper* penny. Copper was used for minting pennies in 1942, but was exchanged for nickel steel in 1943. Activation analysis carried out on the 1943 copper penny showed that the trace elements used in it were identical to those in the 1942 penny. It was therefore concluded that the penny was genuine. There are now known to be five such coins in existence valued at around $50,000 each.

The Availability and Costs of NAA

LAW-ENFORCEMENT LABORATORIES

Most of the preliminary investigations of the possible forensic use of NAA have been carried out either in government laboratories or under research contracts with the Division of Isotopes Development, USAEC. Consequently NAA is already available for law-enforcement agencies on a routine basis through the forensic activation analysis groups in the U. S. Treasury Department, the FBI laboratory of the U. S. Department of Justice, the General Atomic Forensic Activation Analysis Service, and, in Canada, through the Attorney General's Laboratory in Toronto, Ont.

PRIVATE LABORATORIES

In every legal case to date, NAA evidence has been introduced by the prosecutor as an arm of the government, but, if a private individual or his legal counsel should desire to adduce evidence based on NAA, many commercial laboratories offer neutron activation services at nominal cost. Listed in Appendix B are some companies in the United States that offer the service.

COSTS

Many organizations would prefer to keep the responsibilities for forensic analyses within their own confines. For these, the final determining factor is the cost involved, which has to be justified to a governing body. Lenihan[36] has examined cost requirements for organizing and equipping an activation analysis laboratory. In his view, no one need be deterred from this area of work by lack of costly equipment and facilities. Research and routine work in activation analysis may be carried out with equipment costing as little as $1500 or more than $500,000; with minimum laboratory facilities or those ranging upward to the most complex laboratory facilities including a nuclear reactor; and with a staff of only a chemist and technician or a complete ensemble including chemists, reactor operators, computer technicians, physicists, engineers, and technicians. The complexity of the problem to be undertaken will, of course, be decided by the available equipment. The scale of work will be fixed by the organization to fit its budget. With normal air-freight facilities, distances of up to 500 miles from a reactor are not a serious obstacle. Thus activation analysis may easily

become an add-on feature of laboratories already carrying on forensic work by other techniques.

Conclusion

The proponents of forensic NAA, unlike the old-time vacuum cleaner salesmen, make no claim that NAA will do all household chores. Even with the new bag of accessories containing higher neutron fluxes and more sensitive counting arrangements that will extend the number of elements detected and decrease still further the sample size, NAA will remain only a means of elemental analysis. Its use is dictated by and limited to the conditions of the overall problem. The basic information in the related fields of biochemistry, agronomy, and material sciences in many cases is so meager that the accumulation of data and the establishment of norms are required to validate any claimed forensic comparison.

Before NAA is even considered as a tool for helping to solve a particular problem, an interdisciplinary consideration should be given to all aspects of the question. The most careful, precise microanalysis of test specimens is of no value unless it can be shown to be relevant to the solution of the general problem. Then, assuming that NAA is truly applicable to a problem and that the results obtained are scientifically valid, the best use of such testimony in court will be as additional, corroborative evidence to an already well-structured presentation. If properly applied, truly objective and scientifically valid NAA data can best be used as a last bit of evidence to decisively swing the balance in favor of a judgment. In this way the forensic chemist fulfills his obligation to serve society by working in concert with the enforcement agency, yet retains his scientific objectivity and primary obligation to the justice process.

As more materials of evidential interest are studied,[37] the presentations in court continue to accumulate. The merits of specific applications of neutron activation analysis, and the details of methods of analysis, may be argued by the different investigators, but these are just the inevitable difficulties associated with the introduction of a new technique and serve only to enhance the undeniable evidence of its increasing maturity.

Appendix A: List of 17 U. S. Court Cases in Which Activation Analysis Results Were Successfully Introduced

U. S. vs. Anderson et al.
Tried: Mar. 16, 1964
Location: Brooklyn, N. Y., Federal Court
Charge: Conspiracy, violation of Internal Revenue Service laws
Disposition: Guilty
Testimony by: Howard L. Schlesinger, Internal Revenue Service

Neutron activation analysis used for the examination of soil.

U. S. vs. Cornwell
Tried: May 1964
Location: Southern District of Ohio, Federal Court
Charge: Attempted murder
Disposition: Guilty
Testimony by: Howard L. Schlesinger, Internal Revenue Service

Neutron activation analysis used for the examination of automobile body putty and adhesive tape.

California vs. Woodard
Tried: July 1964
Location: California Superior Court, San Mateo County (Redwood City, Calif.)
Charge: Attempted burglary
Disposition: Guilty
Testimony by: Donald E. Bryan, General Atomic

Neutron activation analysis used for the examination of automobile paint.

U. S. vs. Craps, Kneece & Johnson
Tried: Mar. 23, 1965
Location: Aiken, S. C., Federal Court
Charge: Conspiracy, violation of Internal Revenue Service laws
Disposition: Guilty
Testimony by: Maynard J. Pro, Internal Revenue Service

Neutron activation analysis used for the examination of paint.

New Hampshire vs. Coolidge
Tried: May 1965
Location: Manchester, N. H., State Court
Charge: Murder
Disposition: Guilty
Testimony by: C. Michael Hoffman and Maynard J. Pro, Internal Revenue Service

Neutron activation analysis used for the examination of organic and inorganic particles. (Hair—not entered).

U. S. vs. Percy Flowers
Tried: Aug. 16, 1965
Location: Wilmington, N. C., Federal Court
Charge: Conspiracy, violation of Internal Revenue Service laws
Disposition: Acquitted
Testimony by: Howard L. Schlesinger, Internal Revenue Service

Neutron activation analysis used for the examination of soil.

U. S. vs. Asby
Tried: May 20, 1965, and October 16, 1965
Location: Norfolk, Va., Federal Court
Charge: Manufacturing and possession of non-tax-paid whiskey
Disposition: May 20, 1965—Hung Jury
Oct. 16, 1965—Guilty
Testimony by: Howard L. Schlesinger, Internal Revenue Service

Neutron activation analysis used for the examination of soil and grease.

Commonwealth of Virginia vs. Powers
Tried: June 1965
Location: Alexandria, Va., State Court
Charge: Murder
Disposition: Acquitted
Testimony by: Howard L. Schlesinger, Internal Revenue Service

Neutron activation analysis used for the comparison of bullets.

California vs. Herrera
Tried: Oct. 13, 1965, Feb. 2, 1966, and Feb. 7, 1966
Location: Oakland, Calif., State Court
Charge: Aggravated assault and attempted murder
Disposition: Oct. 13, 1965—Hung Jury
Feb. 2, 1966—Defendant Jumped Bail
Feb. 7, 1966—Guilty
Testimony by: C. Michael Hoffman, Internal Revenue Service

Neutron activation analysis used for the examination of soil.

U. S. vs. Johnnie Hall et al.
Tried: December 1965
Location: Clarksdale, Miss., Federal Court
Charge: Conspiracy, violation of Internal Revenue Service laws
Disposition: Guilty
Testimony by: C. Michael Hoffman, Internal Revenue Service

Neutron activation analysis used for the examination of soil.

U. S. vs. Andrew Lee Jackson et al.
Tried: Jan. 31, 1966
Location: Miami, Fla., Federal Court
Charge: Conspiracy, violation of Internal Revenue Service laws
Disposition: Guilty
Testimony by: Maynard J. Pro, Internal Revenue Service

Neutron activation analysis used for the examination of moonshine.

Massachusetts vs. Lisacki
Tried: Apr. 5, 1966
Location: Cambridge, Mass., State Court
Charge: Murder
Disposition: Pled guilty to second degree murder during the trial. Neutron activation analysis was written in the court record.
Testimony by: C. Michael Hoffman, Internal Revenue Service

Neutron activation analysis used for the examination of hair.

U. S. vs. Woodrow Wilson Brogan et al.
Tried: May 9, 1966
Location: Bluefield, W. Va., Federal Court
Charge: Conspiracy, violation of Internal Revenue Service laws
Disposition: Not Guilty
Testimony by: C. Michael Hoffman, Internal Revenue Service

Neutron activation analysis used for the examination of hair.

. S. vs. George Doty et al.
Tried: May 23, 1966
Location: Tulsa, Okla., Federal Court
Charge: Conspiracy, violation of Internal Revenue Service laws
Disposition: Guilty
Testimony by: Maynard J. Pro, Internal Revenue Service

Neutron activation analysis used for the examination of paint.

U. S. vs. Theo Miller Simmons
Tried: June 6, 1966
Location: Gadsden, Ala., Federal Court
Charge: Violation of Internal Revenue Service liquor laws
Disposition: Guilty
Testimony by: C. Michael Hoffman, Internal Revenue Service

Neutron activation analysis used for the examination of paint.

U. S. vs. Jessie McRoy Smith et al.
Tried: June 7, 1966
Location: Washington, N. C., Federal Court
Charge: Conspiracy, violation of Internal Revenue Service laws
Disposition: Smith found guilty—two other defendants to be tried.
Testimony by: Howard L. Schlesinger, Internal Revenue Service

Neutron activation analysis used for the examination of galvanized wire.

Florida vs. Vaughn
Tried: Aug. 10, 1966
Location: Jacksonville, Fla.
Charge: Conspiracy to violate state liquor laws
Disposition: Guilty
Testimony by: Maynard J. Pro, Internal Revenue Service

Neutron activation analysis used for the examination of moonshine.

Appendix B: List of 21 Private Companies Offering Nuclear Activation Analysis Service

Aerojet-General Nucleonics
Box 77
San Ramon, Calif. 93304

Atlantic Research Corp.
Shirley Highway at Edsall Road
Alexandria, Va. 22314

Baird-Atomic, Inc.
33 University Road
Cambridge, Mass. 02138

Controls for Radiation, Inc.
130 Alewife Brook Parkway
Cambridge, Mass. 02140

Edgerton, Germeshausen & Grier, Inc.
Santa Barbara Laboratories Division
Box 98
Goleta, Calif. 93017

General Atomic Division
General Dynamics Corp.
Box 608
San Diego, Calif. 92112

General Electric Company
Industrial Sales Division
1 River Road
Schenectady, N. Y. 12305

General Radioisotope Processing Corp.
3000 San Ramon Valley Boulevard
San Ramon, Calif. 94583

James M. Gerhart
1900 Meadow Lane
Walnut Creek, Calif. 94598

Hazleton-Nuclear Science Corp.
(Subs. Isotopes, Inc.)
4062 Fabian Street
Palo Alto, Calif. 94310

Industrial Reactor Laboratories
Plainsboro, N. J. 08536

Isotopes, Inc.
123 Woodland Avenue
Westwood, N. J. 07675

Kaman Nuclear
Garden of the Gods Road
Colorado Springs, Colo. 80907

Neutron Products Division
Nuclear Utility Services
1730 M Street, N. W.
Washington, D. C. 20036

Nuclear-Chicago Corporation
333 E. Howard Avenue
Des Plaines, Ill. 60018

Nuclear Science and Engineering Corp.
Box 10901
Pittsburgh, Pa. 15236

Tracerlab, A Division of Laboratory for Electronics, Inc.
1601 Trapelo Road
Waltham, Mass. 02154

Tracerlab-Western Division
2030 Wright Avenue
Richmond, Calif. 94804

Union Carbide Corporation
Sterling Forest Research Center
Box 324
Tuxedo, N. Y. 10987

United States Testing Co., Inc.
1941 Park Avenue
Hoboken, N. J. 07030

Westinghouse Electric Corporation
Atomic Power Division
Box 355
Pittsburgh, Pa. 15230

Western New York Nuclear Research Center
Power Drive
Buffalo, N. Y. 14214

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Review of a Report on *Prompt Gamma Rays from Radiative Capture of Thermal Neutrons*

Abstract: A report on prompt-gamma rays from radiative capture of thermal neutrons (IITRI-1193-53, Vols. 1 and 2), prepared by R. C. Greenwood and J. H. Reed, is reviewed. The report contains an atlas of (1) thermal-neutron capture-gamma-ray spectrums measured under standard conditions using NaI(Tl) scintillation detectors and (2) a comprehensive compilation of the neutron capture-gamma-ray data which was available prior to May 1965. Prompt-gamma-ray spectrums and data from more than 70 naturally occurring stable elements, a few naturally occurring radioactive elements, some separated isotopes, and some fissionable materials are given. Also included are the experimental arrangements and procedures for obtaining the neutron flux, neutron cross section, gamma-ray intensities, and spectrum measurements. The objective of this work was to provide sufficient data concerning neutron capture-gamma-ray spectrums to allow evaluation of practical uses of an analytical method based on the detection of neutron capture-gamma rays in measurement, analysis, and control technology and to facilitate the use of such a method in these applications. Sample pages from the atlas are included.

Greenwood and Reed, in work sponsored by the USAEC's Division of Isotopes Development at the Illinois Institute of Technology Research Institute (IITRI), have prepared a report[1] on prompt-gamma rays from radiative capture of thermal neutrons, which contains an atlas of thermal-neutron capture-gamma-ray spectrums and a comprehensive compilation of the neutron capture-gamma-ray data available prior to May 1965. The experimental method, procedure, and apparatus and equipment are described in detail. Included in the atlas are gamma-ray spectrums measured under standard conditions using NaI(Tl) detectors and data from more than 70 naturally occurring elements, a few naturally occurring radioactive elements, some separated isotopes, and some fissionable materials. The quality of this work and the potential applications of the atlas merit review in some detail. Essentially all of the following has been extracted from the report. Sample pages from the atlas showing thermal-neutron reaction processes, effective capture cross sections, tables of both low and high capture-gamma-ray energies, comments, and capture-gamma-ray spectrums are included in the appendix. The report has 302 references and 898 pages. Although the report carries a date of October 1965, it did not become available until early 1967.

When a substance is irradiated with slow (thermal) neutrons, the (n,γ) reaction is generally the only nuclear reaction that can occur. (Exceptions are a few light elements in which alpha particle or proton emission can also occur, and uranium and many of the transuranium elements in which fission is possible.) Following neutron capture, the resulting compound nucleus is in an excited state with energy essentially equal to the neutron binding energy of the compound nucleus — in general, 5 to 8 Mev. Decay occurs promptly — within about 10^{-14} sec — from the excited state to the ground state, normally through several intermediate states, by the emission of gamma rays. In general then, neutron capture-gamma-ray spectrums are complex, consisting of both high- and low-energy gamma radiations.

For a sample which transmits neutrons with little or no attenuation, capture-gamma-ray production is directly proportional to the total neutron capture cross section of the sample. In a sample containing several elements, the quantity σ/A for each element (where σ is the thermal-neutron capture cross section for a particular element and A is its atomic weight) provides an indication of the relative sensitivities for measurement of those elements using a neutron capture-gamma-ray technique. Table 1 shows values of σ/A for the naturally occurring elements

Table 1 VALUES OF σ/A FOR THE NATURALLY OCCURRING ELEMENTS AND THE COMMON FISSIONABLE MATERIALS

σ/A	Element
298	Gd
76	B
10–50	Cd, Sm, Eu
5–10	Dy
1–10	Rh, In, Ir, Hg, ^{239}Pu
0.5–1	Cl, Sc, Co, Ag, Er, Tm, Lu, Hf, Au
0.1–0.5	H, Ti, Mn, Se, Kr, Xe, Cs, Nd, Tb, Ho, Yb, Ta, W, Re, ^{235}U
0.05–0.1	K, V, Cr, Ni, Cu, As, Br, Pd, Lu, Pr, Os
0.01–0.05	Na, S, Ar, Ca, Fe, Zn, Ga, Ge, Sr, Y, Nb, Mo, Ru, Sb, Te, I, Pt, Tl, Th, U, ^{238}U
0.005–0.01	N, Al, Si, P, Rb, Sn, Ba, Ce
0.001–0.005	Li, Be, Ne, Mg, Zr
0.0005–0.001	Pb
0.0001–0.0005	C, F, Bi
<0.0001	He, O

and common fissionable materials. The restricted range of σ/A indicates that a neutron capture-gamma-ray technique is principally a method for macroscopic analysis, trace (ppm) analyses being possible only for a few specialized cases.

Because neutron capture-gamma rays are produced promptly, and there is thus no possibility of using radiochemical separation techniques to improve analytical sensitivity, an analytical method based on measurement of neutron capture-gamma rays is exclusively nondestructive. It is in the field of nondestructive analysis, however, for example, in a quality-control analysis of an on-line process stream, that there exists no single nuclear technique which can be used universally for the solution of all problems in measurement, analysis, and control technology. Instead, there exist several complementary nuclear methods, such as thermal- or fast-neutron activation analysis, inelastic neutron scattering, and neutron capture-gamma-ray analysis, which can be used, depending on the sample under investigation.

Many data already exist in the field of neutron capture-gamma rays. Two original compilations of neutron capture-gamma-ray data, by Groshev et al.[2] and by Bartholomew and Higgs,[3] have been published, as well as a number of excellent review articles, the latest of which were written by Bartholomew[4] and by Motz and Bäckström.[5]

Much of the existing information on neutron capture-gamma-ray energies has been derived using magnetic-pair spectrometers, magnetic Compton spectrometers, or bent-crystal spectrometers. Capture-gamma-ray data obtained with these instruments are extremely valuable in basic studies of nuclear-energy levels. However, these spectrometers are not suitable for most practical applications because of their extremely low gamma-ray detection efficiencies. The relatively low cost and high efficiency provided by scintillation counters are required for the successful use of neutron capture-gamma rays in measurement, analysis, and control technology. Although one can draw inferences from magnetic-pair, magnetic Compton, and bent-crystal spectrometer data, the gross changes in spectrums caused by the reduced resolution, Compton scattering, and other processes peculiar to scintillation counters, make it difficult to use this existing information to evaluate feasibility of a particular application.

Neutron capture-gamma-ray measurements obtained with scintillation detectors have also been reported. However, the diversity of NaI(Tl) crystal sizes and detection conditions used (many times not reported in detail) make the data generally unsuitable for use as reference material for the investigator interested in applying neutron capture-gamma rays to practical problems.

It is the purpose of Greenwood and Reed in their report to provide a comprehensive atlas of both low- and high-energy thermal-neutron capture-gamma-ray spectrums measured under standard conditions, using NaI(Tl) scintillation crystals as detectors; the atlas should be suitable for use as a reference by other investigators interested in practical applications of neutron capture-gamma rays. The availability of this compilation allows a simple paper study to be made of the feasibility of a neutron capture-gamma-ray method for a particular analytical problem.

The first part of the report contains a discussion of the experimental procedures used to measure the thermal-neutron capture-gamma-ray spectrums. In addition, a discussion of the procedures used to provide an energy calibration for these spectrums, to determine the thermal-neutron fluxes at the sample position, and to measure absolute thermal-neutron capture-gamma-ray intensities is included. The thermal-neutron capture-gamma-ray spectrums measured in this work are included in the atlas, together with a compilation of neutron capture-gamma-ray energies and intensities determined both from these spectrums and from spectrums obtained by other investigators. Volume 2 of the report contains the digital data used to prepare the thermal-neutron capture-gamma-ray spectrums shown in Vol. 1. These data permit ready replotting and simulation of spectrums for samples containing a mixture of elements.

Hereafter the terms high- or low-energy spectrums will indicate the high- or low-energy thermal-neutron capture-gamma-ray spectrum unless otherwise stated.

Experimental Arrangement

NEUTRON SOURCE

A collimated beam of neutrons from one of the reactor ports of the IITRI Research Reactor was used to irradiate the samples. This 75-kw homogeneous reactor is fueled with enriched (93%) ^{235}U as a uranyl

sulfate solution. At this power level the thermal-neutron flux in a central exposure position is 1×10^{12} n/(cm^2)(sec).

The criterion used in the selection of a reactor port for these experiments was that the epithermal- and fast-neutron flux and the reactor gamma-ray flux should be minimum relative to the thermal-neutron flux but still retain a usable thermal-neutron flux in the beam. The reason for the selection of this criterion is that both the neutron- and the gamma-beam contaminations can cause serious background problems in the NaI(Tl) scintillation detector. The reduction of the epithermal- and fast-neutron flux is relatively straightforward using any of the reactor ports and is easily accomplished by interposing sufficient moderator between the reactor core and the sample.

The reactor gamma-ray flux results from the fission process itself; the decay of fission products; and neutron capture in the core, the core cladding, the moderator, and the port lining. Reduction of this gamma-ray flux at the sample position proved to be more difficult for a beam emitted directly from the core than for a beam tangential to the core and a few inches from it at the distance of closest approach. Thus a tangential beam was used for these measurements. Gamma rays produced in the core area must undergo Compton scattering before being emitted in the beam. These scattered gamma rays will, in most cases, have energies less than 1 Mev. Since the shielded NaI(Tl) scintillation detector is at an angle of 90° to the neutron beam, such core gamma rays must undergo a second Compton scattering to enter the detector. Consequently, most of the core gamma rays detected by the scintillation detector will have energies less than 350 kev.

Five graphite stringers, each 12 in. long, can be inserted into the moderator region of the beam channel. For the thermal-neutron capture-gamma-ray measurements, three or four of these graphite stringers were generally inserted. In all cases, however, neutrons emitted through the beam port used had traveled through a minimum of 16 in. of graphite and produced a reasonably well-thermalized spectrum.

To obtain good-quality capture-gamma-ray spectrums, a thermal-neutron beam having a minimum cross-sectional area is used. In this way, extraneous background counting effects due to scattering of a large-diameter beam from the shielding, source holder, beam catcher, etc., are minimized. To accomplish this, a collimator with a $^5/_8$-in.-diameter hole was constructed and inserted into the port. For maximum effectiveness, it is necessary to collimate both epithermal and fast neutrons and the reactor gamma rays, as well as the thermal neutrons.

The collimator was constructed from alternate layers of borated paraffin and lead (Fig. 1), the boron collimating the thermal neutrons, and the lead, the gamma rays. The epithermal and fast neutrons were thermalized in the paraffin and captured in the boron. Boron emits only a 477-kev gamma ray when a neutron is captured in the $^{10}B(n,\alpha)^7Li$ reaction (the absorption cross section for natural boron is 752 barns). This gamma ray is easily absorbed by the lead. Lead is a suitable gamma collimator material for this application since it has a low neutron capture cross section; therefore few capture-gamma rays are produced in the lead itself. (Bismuth has an even lower neutron capture cross section but is more expensive.)

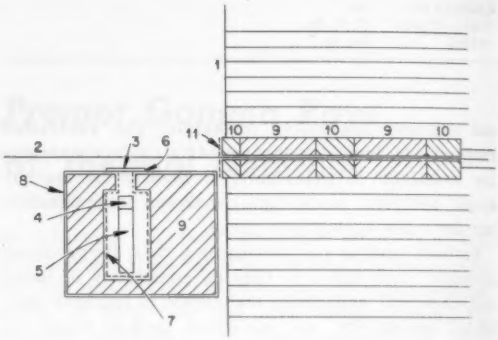


Fig. 1 Neutron collimator and detector arrangement. (1) Reactor; (2) neutron beam; (3) sample; (4) NaI(Tl) crystal; (5) photomultiplier tube and cathode follower; (6) ^{6}LiF disk; (7) graded shield ($^9/_{32}$-in. tin plus $^1/_{64}$-in. copper); (8) boral ($^1/_4$ in.); (9) lead; (10) borated paraffin; (11) cadmium or tin shutter.

A further reduction in the reactor gamma-ray flux relative to the thermal-neutron flux was obtained by placing a $^3/_8$-in.-thick lead filter in the beam at the midpoint of the collimator.

The external reactor beam should be completely absorbed in a beam catcher, with minimum production of high-energy capture-gamma rays and minimum neutron and gamma-ray backscattering into the sample-detector area. Consequently, with the beam catcher that was constructed, the neutron beam travels down a 4-in.-diameter, 15-in.-long hole and into the central region of a borated paraffin block (boric acid was used as the boron-containing medium). The paraffin block is contained in a concrete barrel 30 in. in diameter by 48 in. long, with 3-in.-thick walls. The base of the barrel consists of 19 in. of reinforced concrete and 2 in. of lead to stop the direct gamma-ray flux in the beam.

DETECTION SYSTEM

Scintillation Detectors. In order for this compilation of spectrums to have general utility, only those NaI(Tl) crystal sizes which could be considered standard were used for the measurements. Thus special detectors, such as very large NaI(Tl) crystals

and NaI(Tl) crystals surrounded by large NaI(Tl) annuluses in an anticoincidence arrangement, were not considered.

The criterions that govern the selection of the scintillation-crystal size necessary to obtain good-quality spectrums are at variance for measurements in the low- and high-energy gamma-ray spectral regions. Thus several different crystal sizes are necessary to adequately cover the total region. For the high-energy spectral region, a large NaI(Tl) scintillation crystal is desired because, as the crystal size increases, the full-energy peak becomes more prominent, with a corresponding decrease in the escape peaks and the Compton distribution.

With the low-energy (below 1 Mev) spectrums, the Compton distribution from the higher energy capture-gamma rays sets the lower limit on analytical sensitivities. To reduce this Compton distribution relative to the low-energy capture-gamma-ray peak heights, two conflicting criterions must be satisfied. First, as the scintillation-crystal size is reduced, the ratio of the detection efficiencies of the low-energy gamma rays to those of the high-energy gamma rays is increased. On the other hand, as the crystal size is reduced, the peak-to-total ratios are also reduced, and thus relatively fewer counts from the lower energy gamma rays are contained in the full-energy peaks and relatively more counts from the high-energy capture-gamma rays are contained in the background Compton distribution. A series of experiments with a variety of crystal sizes shows that a 1.5- by 1-in. NaI(Tl) crystal is about the minimum size that can be used to obtain reasonable neutron capture-gamma-ray spectrums over the whole low-energy spectral region.

Therefore the low-energy spectrums were measured with 1.5- by 1-in. and 3- by 3-in. NaI(Tl) crystals, while 3- by 3-in. and 5- by 4-in. NaI(Tl) crystals were used to measure the high-energy spectrums. Details of the scintillation detectors used and their energy resolutions are shown in Table 2.

Table 2 SCINTILLATION DETECTORS USED TO MEASURE THERMAL-NEUTRON CAPTURE-GAMMA-RAY SPECTRUMS

Scintillation-crystal size, in.	Photomultiplier tube	Crystal backcap thickness, in.	Energy resolution, %	
			At 661.6-kev ^{137}Cs line	At 477-kev $^{10}B(n,\alpha)^{7}Li$ line
1.5 by 1	RCA 6342A	0.109	7.00	8.26
1.5 by 1	RCA 8053	0.133	7.60	8.88
3 by 3	DuMont 6363	0.266	7.25	8.45
5 by 4	RCA 8055	0.225	7.25	8.79

The 1.5- by 1-in. NaI(Tl) detector, which had the better energy resolution, was used to measure spectrums from the great majority of the elements in this compilation. This crystal, however, was accidentally broken before the completion of the program, and a slightly inferior 1.5- by 1-in. NaI(Tl) crystal was used to obtain spectrums from the remaining few elements. The variation in detector resolution as a function of gamma-ray energy is shown in Fig. 2 for the better 1.5- by 1-in. NaI(Tl) detector and for the 3- by 3-in. NaI(Tl) detector.

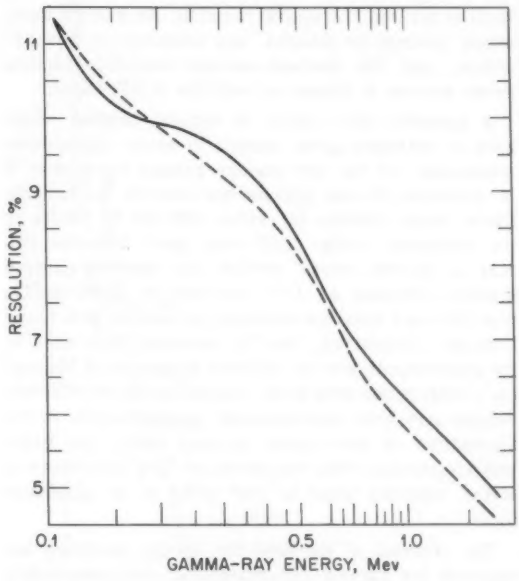


Fig. 2 Energy resolution of the NaI(Tl) scintillation detectors; 1.5 by 1 in. (dotted line), 3 by 3 in. (solid line).

The positive high voltage to the dynode bleeder chain on the photomultiplier tubes was supplied from a Hamner Electronics Co., Model N-401, power supply. The output pulses from the anode of the phototube, after passing through a White cathode follower, were analyzed in a Nuclear Data, Inc., Model ND-130, 512-channel pulse-height analyzer.

Detector Shield Arrangement. Figure 1 shows a cross-sectional diagram of the NaI(Tl) detector together with its associated shielding in position at the reactor face. The lead detector shielding (minimum thickness 2 in.) was in turn shielded by $\frac{1}{4}$-in. boral sheet that contained 35% boron carbide. With this shielding arrangement thermal neutrons scattered from the beam were prevented from being captured in the lead shield with the resultant emission of 7.38-Mev capture-gamma rays. Instead, such scattered thermal neutrons were absorbed by the boron, with the resultant 477-kev prompt-gamma rays from the $^{10}B(n,\alpha)^{7}Li$ reaction being absorbed by the lead. A gamma collimator hole in the lead shield was in the direct path between the sample and the NaI(Tl) crystal.

Since there is an appreciable neutron scattering by the samples, a neutron filter must be placed in front of the collimator. Boron is not a suitable filter because the 477-kev prompt-gamma rays emitted as a result of neutron absorption would obscure the low-energy spectrums measured with this system. Lithium, however, is ideal for this filter because the ^{6}Li isotope has a 950-barn thermal-neutron cross section for the $^6Li(n,\alpha)^3H$ reaction. No gamma rays, either prompt or delayed, are produced in this reaction, and the thermal-neutron radiative-capture cross section of lithium is very low (0.071 barn).

A neutron filter made of natural lithium would have a thickness great enough to cause appreciable attenuation of the low-energy gamma rays; thus it is desirable to use lithium enriched in ^{6}Li for this filter. Since lithium is rather difficult to handle in its elemental state, ^{6}LiF was used. Fluorine has only a 10-mb cross section for thermal-neutron capture. Lithium as LiF, enriched to 95.6% in ^{6}Li, was obtained from the Isotopes Division of Oak Ridge National Laboratory. The ^{6}Li neutron filter used in the experiments had an effective thickness of 764 mg/cm^2, determined both from considerations of effective density and from experimental measurements of the attenuation of low-energy gamma rays. The filter was constructed with the powdered ^{6}LiF held between Mylar windows glued to both sides of an aluminum form.

The interior of the detector shield, including the walls of the gamma-ray collimator, was lined with a graded shield consisting of $^3/_{32}$-in. tin plus $^1/_{64}$-in. copper. The purpose of this shield was to prevent the lead K X rays produced in the lead shield from being detected by the NaI(Tl) crystals. The detector cavity in the shield was 7.5 by 7.5 by 17 in.

A different size of gamma collimator in the detector shield was used for each of the three NaI(Tl) crystal sizes. For the 1.5- by 1-in. crystal, the collimator hole had a diameter of 1.5 in., while, for the 3- by 3-in. and 5- by 4-in. NaI(Tl) detectors, cone-shaped collimators were machined in 2-in.-thick lead bricks with dimensions of $3^{11}/_{16}$ in. tapering to $1^{15}/_{32}$ in. and $4^7/_8$ in. tapering to $2^1/_4$ in., respectively. These tapered collimators were designed so that a $^5/_8$-in.-diameter source, at a crystal backcap-to-sample distance at about 4 in., could see all the crystal.

In practice, an average crystal backcap-to-sample distance of 4.15 in. was used to obtain the spectrums. Maximum variations in this distance over the complete set of measurements was less than ±0.14 in., and, for all but a few spectrums, the variation was less than ±0.10 in.

SAMPLES

Most of the samples of the naturally occurring elements were obtained in spectroscopically pure grades through the Jarrell-Ash Co., Waltham, Mass., from Johnson, Matthey & Co., Ltd., London, England. Of the remaining stable elements, seven (B, Na, Nb, I, Tl, Pb, and Bi) were obtained in the highest purities available from Light and Co., Ltd., Colnbrook, Bucks, England, and four (H, Be, Zr, and Y) were obtained in very high purities from other sources.

Although most of the samples used were of a spectroscopically pure grade, care was still necessary in the interpretation of neutron capture-gamma-ray data measured with these samples because not all the possible impurities were determined spectroscopically, e.g., the halogens and the rare-earth elements (except as impurities in the rare-earth elements and other Group IIIB elements). The rare-earth elements, however, would be expected to provide significant contaminations only to the Group IIIB elements. This was confirmed by a series of simple activation analyses to determine limits on the dysprosium and europium contents of some of the low neutron capture-cross-section samples (Table 3).

Table 3 MEASURED DYSPROSIUM AND EUROPIUM IMPURITY CONTENTS OF SPECTROGRAPHICALLY PURE SAMPLES

Samples	Content, ppm	
	Dysprosium	Europium
B	<0.4	<1.4
Na_2CO_3	<1.7	<43
Mg	<0.068	<0.020
Al	<0.069	<0.014
Si	<0.18	<0.034
S	<0.008	<0.009
K	<1.0	<10
Ca	<0.10	<0.080
Fe	<0.071	<0.75
Zn	<2.1	<5.9
Ga	<37	<57
Sr	<2.0	<15
Y	<0.54	<2.2
Zr	<0.21	<0.36
Nb	<0.20	<0.75
Sn	<2.7	<0.15
Te	<3.0	<22
Ba	<4.5	<75
La	≤56*	<160
Ce	<0.30	<7.7
Pr	<12	<120
Tb	67	<26
Ho	<120†	<700
Tl_2O_3	<0.21	<0.068

*This upper limit is probably correct for the dysprosium.
†Most of the ^{165m}Dy activity is produced by the ^{165}Ho(n,p)^{165m}Dy reaction; emission-spectrographic analysis for dysprosium showed less than 50 ppm.

The activation analysis experiments were optimized for the detection of dysprosium, so that the upper limits on the europium content shown in Table 3 are higher than those for dysprosium. However, for other than rare-earth samples, the odd–even rule indicates that the europium impurity content would always be less than the dysprosium impurity content because the natural rare-earth ratios would remain unchanged in the separation and purification processes applied to the sample.

No values for the halogen contents of the samples were available, but neutron capture-gamma-ray spectrums of several of the carbonates and oxides showed significant chlorine contamination. Whenever chlorine contamination was observed in the spectrums, the measurements were repeated with a new sample.

In general, it was necessary to use a compound that contained the element of interest as the sample for measurement. Because oxygen, carbon, and fluorine have very low thermal-neutron capture cross sections, the most suitable compounds were oxides, carbides, carbonates, and fluorides. The technique used to prepare samples for irradiation in the neutron beam was to compact either the powdered compounds or the elements, using a simple die, into uniformly thick $^5/_8$-in.-diameter disks, contained in 99.99% pure aluminum foil. Great care was taken in this procedure not to contaminate the samples. For a thin sample, 0.001-in.-thick aluminum foil was used for the container. As an added precaution against leakage, each sample was doubly contained by the foil. The total mass of aluminum in the container for a thin sample was about 40 mg.

To reduce the background effects, the samples were suspended in the neutron beam on a set of fine tungsten cross wires. In this way, materials in the neutron beam other than the sample of interest were kept to a minimum. The cross wires were supported on a rigid aluminum frame, which could easily be moved into or out of the neutron beam with the reactor at full power. The angle between the plane of the sample and the neutron beam averaged about 40°.

Experimental Procedure

BACKGROUND

Despite the careful design of the experimental system, an appreciable background counting rate was still shown by the NaI(Tl) detector even when no sample was in the beam. The low-energy background spectrum (Fig. 3) was measured with only an empty aluminum sample container in the beam. The background counting rate observed under these conditions with the 3- by 3-in. NaI(Tl) detector was approximately 3.3×10^3 counts/sec, depending on the exact neutron flux.

As an aid to interpreting the structure observed in Fig. 3, one can compare this spectrum to that of iodine shown in Fig. 4 (from the atlas). After allowance for the gamma-ray self-absorption in the 1.0023-g iodine sample used to measure the spectrum in Fig. 4, it appears reasonable on the basis of this comparison to assign the 28- and 134-kev lines to iodine neutron capture-gamma-ray origin. (The 28-kev line would therefore be the iodine K X-ray line.) The presence of iodine neutron capture-gamma rays in the background spectrum is not unexpected since scattered neutrons incident on the NaI(Tl) detector would be principally absorbed by the iodine. The thermal-neutron absorption cross section for iodine is 6.4 barns compared to 0.53 barn for sodium, and iodine has a number of strong capture resonances in the energy region from 20 to 200 ev.

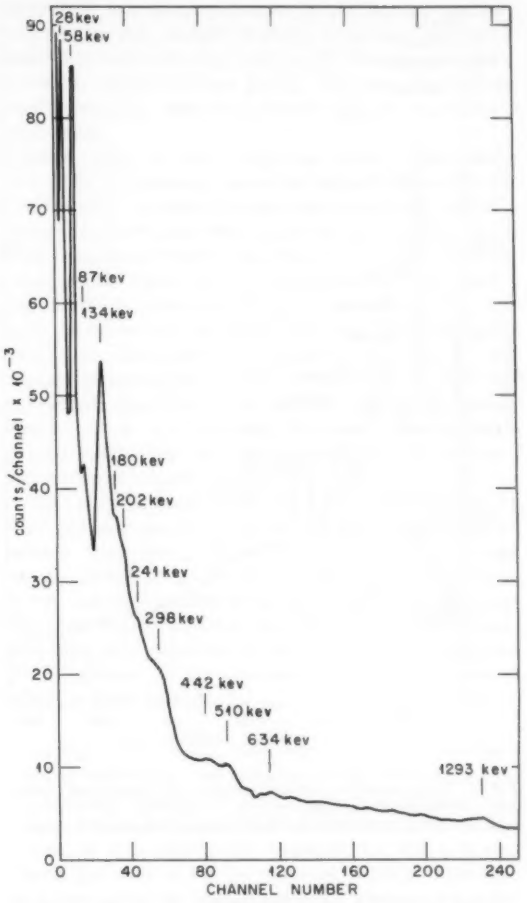


Fig. 3 Low-energy background spectrum. Sample, none; crystal, 3- by 3-in. NaI(Tl); live count time, 20 min; neutron flux, 2.94×10^6 n/(cm²)(sec).

In the other line structure visible in Fig. 3, the weak 87-kev line will undoubtedly contain a strong, if not dominant, contribution from the 91-kev sodium neutron capture-gamma rays. The strong 58-kev line, however, does not appear to be explainable as a neutron capture-gamma-ray line. Instead, the only feasible interpretation for this 58-kev line is that it is produced as a result of inelastic scattering of fast neutrons in iodine. (The first excited state of ^{127}I is at 59 kev.) Because of the lack of more definitive evidence, however, this latter assignment can be made only tentatively.

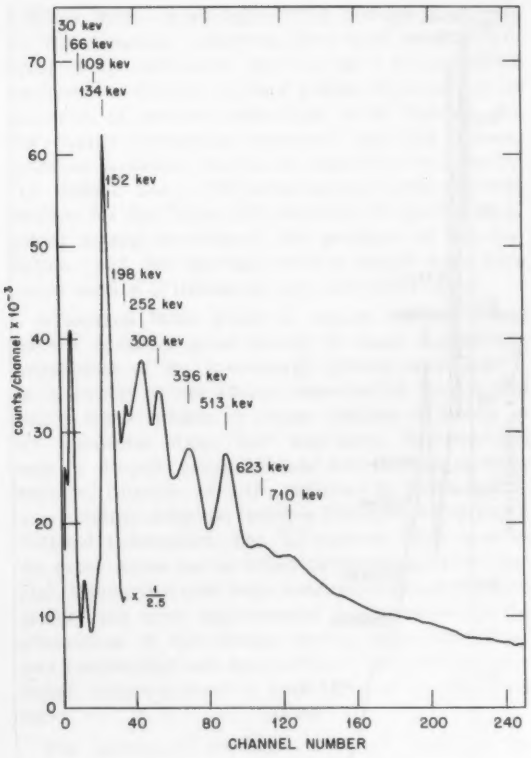


Fig. 4 Iodine neutron capture-gamma-ray spectrum. Sample, 1.0023-g iodine flake; crystal, 3- by 3-in. NaI(Tl); neutron flux, 3.39 × 10⁶ n/(cm²)(sec); live count time, 20 min.

Since scattered neutrons appear to be the cause of most of the background structure observed in Fig. 3, the contribution of the long-lived reaction products resulting from neutron capture in the NaI(Tl) crystal must also be considered:

$$^{23}Na(100\%)(n,\gamma)^{24}Na(\sigma = 0.534 \text{ barn}) \xrightarrow{15 \text{ hr}, \beta^-} {}^{24}Mg \text{ (stable)}$$

$$^{127}I(100\%)(n,\gamma)^{128}I(\sigma = 6.6 \text{ barns}) \xrightarrow[EC(6.5\%)]{25 \text{ min}} {}^{128}Te \text{ (stable)}$$

$$\xrightarrow[\beta^-(93.5\%)]{25 \text{ min}} {}^{128}Xe \text{ (stable)}$$

The beta rays (maximum energy 2.12 Mev) emitted in ^{128}I decay will therefore contribute significantly to the background spectrum. The 442-kev line observed in Fig. 4 probably also results from ^{128}I decay. Consistent with the expectation that this ^{128}I activity would provide an observable contribution to the background, it is noted that, for the first hour or so after the neutron beam is turned on, the background counting rate builds up until equilibrium is reached. The spectrum shown in Fig. 3 was measured at this equilibrium background level. The contribution to the background spectrum from the ^{24}Na activity, even at equilibrium, would be much less than that from the ^{128}I activity and thus is probably negligible.

When a sample is introduced into the beam, epithermal neutrons, fast neutrons, and reactor gamma rays scattered from the sample will also contribute to the background spectrum measured by the NaI(Tl) crystal. These effects will be particularly significant for elements that have small thermal-neutron capture cross sections and thus necessitate the use of samples with large masses.

BACKGROUND CORRECTION

The uncorrected capture-gamma-ray spectrum measured with a sample in the neutron beam also contains contributions from the diverse background effects discussed briefly in the preceding section. In this section of the report, Greenwood and Reed give an extensive description of their background correction method. They consider 11 background effects, i.e., various combinations of thermal, epithermal, and fast neutrons producing gamma rays from capture and inelastic scatter from the sample, sample holder, shielding, etc., as well as beam gamma rays scattered from these objects.

Two of the 11 background effects are related to the scattering of capture-gamma rays produced in the cadmium shutter used in determining sample spectrums. Cadmium is the most suitable material for the thermal-neutron shutter because its neutron reaction cross section contains essentially a step function around 0.4 ev. It has a high thermal-neutron reaction cross section, greater than 2400 barns at energies less than 0.25 ev, which decreases sharply to 300 barns at 0.4 ev, and 22 barns at 1.0 ev. Thus the 335-mg/cm²-thick cadmium shutter will transmit less than 1.1% of the neutrons with energies below 0.25 ev, 57% of the 0.4-ev neutrons, and more than 96% of the neutrons with energies greater than 1.0 ev.

The procedure developed to compensate for background in the measured spectrums was predicated on the assumption that cadmium filter attenuations of the epithermal-neutron, fast-neutron, and reactor gamma-ray fluxes in the reactor beam were negligible. Nevertheless, because the average energy of the reactor gamma rays in the beam is low, the cadmium filter does attenuate this reactor gamma-ray flux by a few percent. This attenuation has little effect on the prompt-gamma-ray spectrums measured with samples of high thermal-neutron capture cross sections; however, with samples of low thermal-neutron capture cross sections, the sample sizes required for measurement are larger, and the scattering of the reactor gamma rays by the sample becomes significant.

The reactor gamma rays Compton-scattered out of the neutron beam by the cadmium filter can be completely compensated for by inserting a 335-mg/cm².

thick tin filter (i.e., of the same thickness as the cadmium filter) in the neutron beam when the cadmium filter is not used. With this arrangement, the tin and cadmium filters attenuate the reactor gamma rays in the beam equally so that compensation is complete in the final capture-gamma-ray spectrums for the reactor gamma rays that are Compton-scattered from the sample into the NaI(Tl) crystal. The tin filter will, of course, attenuate the thermal-neutron beam only slightly, while the two filters will attenuate the fast-neutron beam about equally (this attenuation is small — somewhat less than 1%).

Four spectrums were measured for each sample to obtain the thermal-neutron capture-gamma-ray spectrums shown in the atlas. The conditions for measuring the four spectrums were, respectively:

1. Sample in the neutron beam, with a 335-mg/cm^2-thick tin filter located in the beam at the reactor face
2. Sample in the beam, with the thermal neutrons removed from the beam by a 335-mg/cm^2-thick cadmium shutter located in the beam at the reactor face
3. Sample removed from the beam (but with the sample holder and an equivalent empty aluminum sample container in the beam), with the cadmium shutter still in the neutron beam
4. Sample removed from the beam (but again with the sample holder and the empty aluminum container in the beam), with the tin filter in the beam

The thermal-neutron capture-gamma-ray spectrum of the sample is then obtained from

$$(\text{Sample thermal-neutron capture-gamma rays}) = 1 - 2 + 3 - 4 \quad (1)$$

The calculation required by Eq. 1 was performed in the 512-channel Nuclear Data analyzer by storing data in two sets of 256 channels and using the stripping and negative addition features of the analyzer.

The procedure described by Eq. 1 for measuring the spectrums was first suggested by Hamermesh and Hummel,[6] and the spectrums measured using Eq. 1 are really "sub-cadmium" neutron capture-gamma-ray spectrums. With the cadmium filter thickness used in this work, the average cadmium cutoff energy is 0.45 ev.

Although the thermal-neutron capture-gamma-ray spectrums in the atlas were measured by the procedure described by Eq. 1, it is of interest that, if only the first two spectrums are used and capture-gamma rays produced in the cadmium shutter are neglected (their contribution to the final spectrum should be negligible with the present experimental arrangement), the equation becomes

$$(\text{Sample thermal-neutron capture-gamma rays}) + b = 1 - 2 \quad (2)$$

where b = prompt-gamma rays from thermal-neutron capture in the sample holder, shielding, etc. In a relatively well-designed system, the background contribution from b will be small, and thus reasonably good spectrums may be obtained with this simplified procedure.

Since many of the background effects principally affect the low-energy spectral region, especially the troublesome reactor gamma-ray scattering effects, an uncorrected high-energy spectrum (i.e., the spectrum measured under condition 1) can still provide considerable detail. This is illustrated by a comparison of the uncorrected titanium spectrum (Fig. 5*a*) with the corrected spectrum from the atlas (Fig. 5*b*). The whole line structure observed in Fig. 5*b* (the corrected spectrum) is also seen in Fig. 5*a* (the uncorrected spectrum), but without quite the same clarity. Thus, for elemental analyses using the high-energy spectrums, the uncorrected prompt-gamma-ray spectrums alone can often be used.

The measurement procedure described by Eq. 1 does not necessarily remove all the background resulting from the production of the 25-min ^{128}I beta decay activity in the NaI(Tl) crystal. This ^{128}I activity in the crystal results from the epithermal and fast neutrons scattered from the sample, sample holder, shielding, etc., into the crystal. The authors describe their method of compensation of this background effect in their report.

Energy Calibration. An energy calibration for each sample spectrum was obtained from measurements of selected calibration spectrums both immediately before and immediately after the measurement of the series of four spectrums required for Eq. 1. It was found that line energies could be readily measured with an error of less than 1.0% using a rapid and quite simple calibration procedure.

A key feature of the energy calibration procedure was the use of neutron capture-gamma-ray lines from selected elements as energy standards, in addition to standard lines from radioactive sources. The use of capture-gamma-ray lines in the calibration procedure allowed for a more complete coverage of the energy regions of interest. In addition, because several of the capture-gamma-ray spectrums selected contained more than one line that could be used for calibration, fewer individual calibration measurements were necessary.

In the low-energy spectral region, i.e., the energy region below about 1.4 Mev, until recently cadmium and gold were the only two elements for which precise energy measurements of the capture-gamma-ray lines existed. The capture-gamma-ray spectral structure of gold, however, is not really suitable for use as an energy calibration standard with spectrums measured using NaI(Tl) scintillation detectors. Thus it was necessary to produce a set of neutron capture-gamma-ray energy standards for use in calibration.

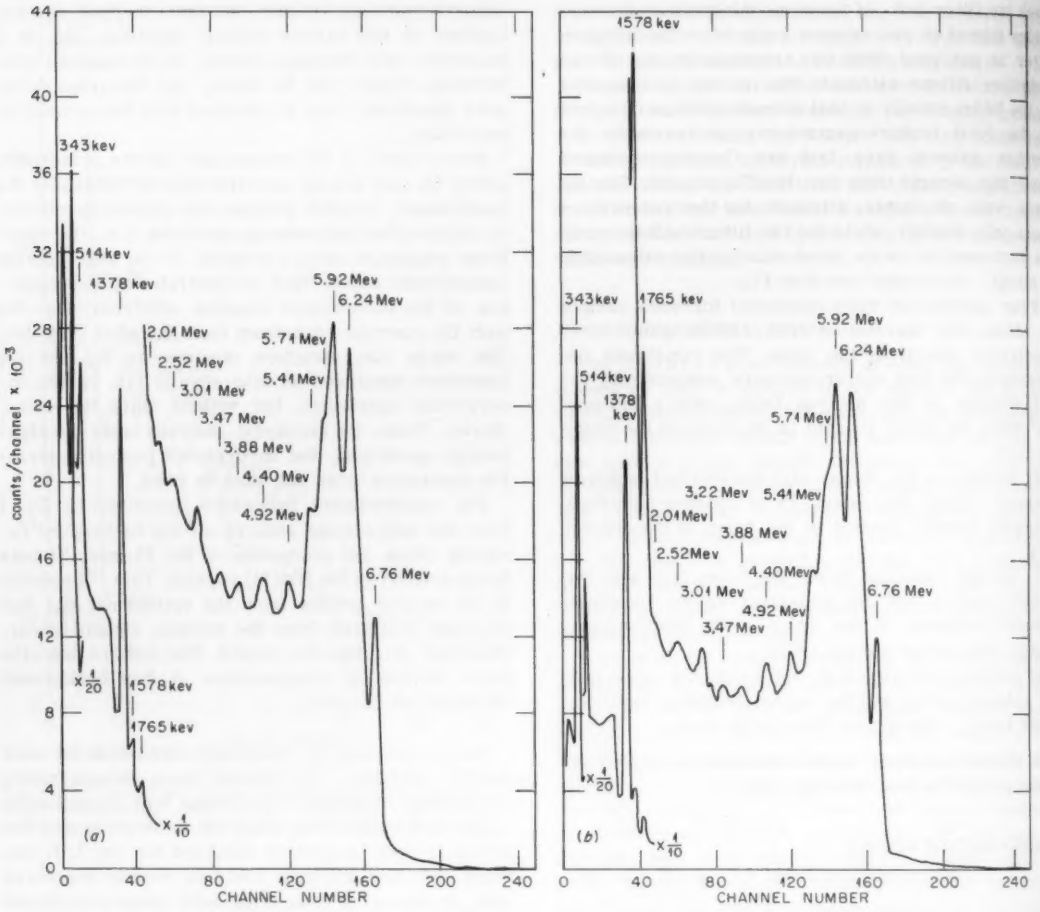


Fig. 5 Titanium spectrums (a) uncorrected and (b) corrected. Sample, 500-mg titanium sponge; crystal, 3- by 3-in. NaI(Tl); neutron flux, 3.39 × 10^6 n/(cm^2)(sec); live count time, 20 min.

Rhodium, samarium, and boron were observed to have a prominent low-energy line structure that appeared suitable for energy calibration standards. For calibration purposes, only the first two spectrums required for Eq. 1 were measured, the thermal-neutron capture-gamma-ray spectrums being determined from

(Sample thermal-neutron capture-gamma rays) = 1 − 2 (3)

Thirteen standard energy lines from several radionuclides and from the Cd(n,γ) reaction, which were used for calibrating the rhodium, samarium, and boron prompt-gamma-ray spectrums, are listed in the report. In making an energy calibration "run" of each of these three elements, calibration lines were measured both before and after each of the sample prompt-gamma-ray spectrums. In this way, gain shifts due to both long-term drifts and the count-rate dependence of the phototube gain could be observed and corrections applied. The energies measured for the prominent low-energy lines in rhodium, samarium, and boron are shown in Table 4 for four separate sets of runs. Internal consistency was good among the energies measured for each line in the four runs. The average value of 477 kev obtained for the ^{7}Li gamma ray is in excellent agreement with the value of 477.3 kev measured by DuMond.[7] Measurements of the samarium lines made by Bieber et al.[8] indicate the values of the two prominent lines to be 333.945 ± 0.015 kev and 439.398 ± 0.020 kev. Thus the line energies for boron and samarium used for calibration in this work show a maximum variation of only 0.6% from the precise values of DuMond and Bieber et al. The complete set of standard lines used for

Table 4 MEASURED NEUTRON CAPTURE-GAMMA-RAY ENERGY STANDARDS

Sample	Energy determination, kev				
	First	Second	Third	Fourth	Average
Rhodium	51.8	50.7	51.6	51.8	51.5
	98.1	97.0	96.5	97.0	97.2
	134.0	134.0	132.2	132.6	133.2
	181	182	181	181	181
	218	219	216	216	217
Samarium	338	335	335	334	335.5
	444	443	441	440	442
Boron, in the $^{10}B(n,\alpha)^7Li$ reaction	480	478	476	475	477

energy calibrations of both the low- and high-energy thermal-neutron capture-gamma-ray spectrums is given in the report. Line energies range from 20.16 kev to 9.298 Mev.

Because the calibration curve appeared to be quite linear in the high-energy region, fewer standard calibration lines were necessary there, and a significant energy gap between the 2.22318-Mev hydrogen and the 5.965-Mev iron capture-gamma-ray line is quite acceptable. Even with few standard energy calibration points, capture-gamma-ray line energies were measured with an accuracy of much better than 1.0% in the higher energy spectral region.

THERMAL-NEUTRON-FLUX MEASUREMENTS

The method for measuring the thermal (sub-cadmium) neutron flux of the reactor beam took advantage of the large neutron-absorption cross section of boron and the accurately known production rate of 477-kev prompt-gamma rays in the resultant $^{10}B(n,\alpha)^7Li$ reaction. Because of boron's high neutron-absorption cross section, more than 99% of the sub-cadmium neutrons can be absorbed in a relatively thin boron sample. Furthermore, the measurements of De Juren and Rosenwasser[9] indicate that the 477-kev excited state of ^7Li occurs in 93.48 ± 0.05% of all the $^{10}B(n,\alpha)^7Li$ reactions resulting from thermal-neutron absorption. Therefore, by absorbing essentially all the sub-cadmium neutrons in a "thick" boron sample, it is possible to measure the "true" sub-cadmium neutron flux without knowing the average boron absorption cross section for sub-cadmium neutrons.

Boron carbide disks contained in a $\frac{1}{16}$-in.-thick aluminum form, constructed in the same manner as that for the ^6LiF screen, were used for these flux measurements. Three such boron carbide disks with diameters of 0.170, 0.284, and 0.627 in. were used. The thickness of each disk was about 220 mg/cm^2.

A sample holder with tungsten cross wires was used to position the boron carbide disk samples in the neutron beam. The boron carbide samples were set in the neutron beam at an angle, θ (on the average about 40°), to the direction of the neutron beam. The sub-cadmium neutron flux was obtained from measurement of the intensity of the 477-kev gamma-ray line resulting from the $^{10}B(n,\alpha)^7Li$ reaction, residual from the four-step subtraction procedure described by Eq. 1.

If each boron carbide disk could be considered infinitely thin relative to the diameter of the disks, the effective area of boron samples exposed to the neutron beam would be expressed as

$$A_b = \frac{\pi}{4} a^2 \sin\theta \qquad (4)$$

where a is the diameter of the boron carbide sample. Instead, however, the boron carbide samples had a finite thickness, and Greenwood and Reed present calculations for compensating the total edge-effect correction and then the effective area of the boron carbide samples exposed to the neutron beam. The edge-effect correction is relatively large for the small boron carbide disk but quite small with the large one. The validity of the edge-effect correction was confirmed by the excellent agreement obtained for thermal-neutron-flux values measured with the small, medium, and large boron carbide disks.

The effective areas computed for the small and medium boron carbide samples seen by the neutron beam were relatively insensitive to θ in the range 34 to 42°. An accuracy of ±0.5° in the measurement of θ was more than adequate.

The medium-size boron carbide disks were used exclusively to measure thermal-neutron fluxes with the 1.5- by 1-in. NaI(Tl) crystal, while the small sample was used with both the 3- by 3-in. and the 5- by 4-in. NaI(Tl) crystals.

The true sub-cadmium neutron flux, F, was obtained from measurements with the thick boron carbide samples using the expression

$$F = N_b/0.9348\ \epsilon_b P_b A_b S_b (T_a)_b (T_b)_b$$

where N_b = count rate measured in the 477-kev full-energy peak

ϵ_b = absolute detection efficiency for the 477-kev gamma radiation

P_b = peak-to-total ratio for the 477-kev gamma rays

S_b = a factor that accounts for the self-absorption of the 477-kev gamma rays in the boron carbide samples = essentially 1.000 because these gamma rays are produced close to the front surface of the boron carbide disks

$(T_a)_b$ = relative transmission of the 477-kev gamma rays through the ^6LiF screen

$(T_b)_b$ = relative transmission of the 477-kev gamma rays through the backcap material of the NaI(Tl) crystal

It is these true sub-cadmium fluxes which are shown on each figure in the atlas.

PROCEDURE USED TO MEASURE THE ATLAS SPECTRUMS

The sequence of measurements routinely used to obtain both the high- and low-energy spectrums shown in the atlas are given in detail in the report. In brief, measurement of high-energy spectrums involved, besides the four spectrums for the sample, determining, both before and after the sample spectrums, (1) the capture-gamma-ray spectrums of iron and of hydrogen in a Lucite sample and (2) the energy spectrum of ^{60}Co gamma emission. The sub-cadmium flux of the beam at the sample position was also determined. In a normal operating day, the high-energy spectrums from two different samples were generally measured.

The procedure for measuring the low-energy spectrums was more involved. Although iron spectrums were not made, capture-gamma-ray spectrums for rhodium, samarium, and cadmium and gamma-ray spectrums of ^{60}Co and ^{137}Cs were made both before and after the four sample spectrums. With the 1.5- by 1-in. NaI(Tl) scintillation detector, the spectrum from only one sample could be measured in a normal operating day; with the 3- by 3-in. NaI(Tl) detector, two spectrums could usually be measured in 1 day. When the larger detector was used, fewer steps were repeated with the second sample if the energy scale remained unchanged.

An experimental measurement of the Compton continuum level in the energy region below 100 kev is helpful in the spectral stripping procedure that must be undertaken to determine neutron capture-gamma-ray intensities. Thus, in addition to the normal low-energy spectrum, a second spectrum is obtained having a $\frac{3}{32}$-in. tin plus $\frac{1}{64}$-in. copper filter inserted between the sample and the NaI(Tl) crystal to completely absorb the capture-gamma rays with energies less than about 100 kev. Therefore the resultant capture-gamma-ray spectrum in the region below 100 kev contained only the Compton continuum from the higher energy capture-gamma rays. In determining the general compton continuum level below 100 kev from these data, a small correction was necessary for attenuation of the higher energy gamma rays by the tin and copper filter.

Neutron Flux and Neutron Capture Cross Sections

The report stresses that an understanding of the proper uses of neutron fluxes and neutron capture cross sections is essential for their correct use in the computation of thermal-neutron capture-gamma-ray intensities. It appears however, from the published literature on neutron capture-gamma rays, that in several of the papers the capture-gamma-ray line intensities were computed using an incorrect definition of neutron capture cross section. The two most common types of improper usage were (1) in conjunction with the true neutron flux in an equation to compute absolute capture-gamma-ray intensities and (2) in the calculation of intensities from a sample which has a neutron capture cross section that does not follow the $1/v$ law.

In the report the definition and the application of neutron fluxes and neutron capture cross sections are discussed.

Neutron Capture-Gamma-Ray Intensity Measurements

For maximum flexibility in the use of the atlas, it is desirable to have available the absolute intensities of the neutron capture-gamma rays. The availability of these intensities will enhance the usefulness of the atlas for practical applications by allowing corrections for gamma-ray self-absorption effects (in the diversity of sample sizes and types considered for analysis) to be made more easily for the assessment of feasibility. Gamma-ray self-absorption effects are particularly important for low-energy-neutron capture-gamma rays, especially when the matrix material has a high atomic number.

Because of the sensitivity of the low-energy spectrums to sample self-absorption effects, detailed analyses were made with the low-energy spectrums measured for the atlas to obtain absolute line intensities in addition to line energies. Such comprehensive analyses for line intensities were not, however, attempted with the high-energy spectrums because:

(1) Sample self-absorption effects influenced the high-energy spectrums much less.

(2) The high-energy spectrums were, in general, much too complex to allow meaningful intensity analyses to be made from spectrums measured with a simple NaI(Tl) scintillation spectrometer.

(3) The magnetic Compton and pair spectrometer data were much superior to the spectral data obtained with a NaI(Tl) scintillation spectrometer because of the better energy resolution and "cleaner" spectral response of the magnetic Compton and pair spectrometers (only full-energy peaks are observed with these magnetic spectrometers, while the sum of the full-energy peak, the escape peaks, and the Compton distribution is obtained from the scintillation spectrometers).

Instead, absolute intensities of only the highest energy lines (i.e., with energies equal to or just less than the energies of the capturing states) were measured in this work.

Neutron Capture-Gamma-Ray Line Assignments and Intensity Measurements

Comprehensive analyses to obtain line intensities, in addition to line energies, from the high-energy spectrums were not attempted. All that was generally

desired of the high-energy spectrums measured was that capture-gamma-ray energy assignments could be made for comparison with the magnetic Compton and pair spectrometer data.

Analysis of the high-energy spectrums to identify capture-gamma-ray energies is complicated by strong annihilation-radiation escape-peak structure. For a 3- by 3-in. NaI(Tl) scintillation detector, the first escape peak becomes stronger than the full-energy peak at about 3.7 Mev, while the second escape peak also becomes stronger than the full-energy peak with gamma-ray energies in excess of 4.8 Mev. Thus, with a complex high-energy spectrum, it is sometimes difficult to say whether a particular line is accounted for completely by escape-peak structure, or whether it also contains a contribution from a full-energy capture-gamma-ray line. Experimental and computed pulse-height spectrums for high-energy gamma rays detected in a 3- by 3-in. NaI(Tl) crystal are shown in a report by Zerby and Moran.[10] These spectrums proved to be of considerable help in the present spectrum-unscrambling process. In addition, comparison of a high-energy spectrum measured with the 3- by 3-in. NaI(Tl) detector with that measured with the 5- by 4-in. NaI(Tl) detector often allowed more definitive neutron capture-gamma-ray line assignments to be made.

The high-energy capture-gamma-ray line assignments based on these NaI(Tl) scintillation spectral data, while not so complete, were generally in excellent agreement with the magnetic Compton and pair spectrometer data. In addition, it was possible with some elements to identify high-energy capture-gamma-ray lines which had not previously been observed.

The absolute capture-gamma-ray intensity values, determined from the low-energy spectrums contained in this atlas, have generally been found to be in reasonable agreement with the more recent intensity measurements made by other investigators. In several reported studies, where low-energy spectrums were measured using NaI(Tl) scintillation detectors, the discussion given of the procedure used to determine the absolute capture-gamma-ray intensities indicates that the intensity values were computed incorrectly. In such cases the basic technique used to measure absolute capture-gamma-ray intensities was similar to that used in this work; but, instead of using the equation given in the report (Eq. 35 in Ref. 1) to measure intensities, a somewhat different equation was apparently used. The text of the report gives the equations and discusses the differences.

One of the principal hindrances to a critical evaluation of the capture-gamma-ray intensity values quoted by different investigators is that many of the papers reporting these data contain insufficient or even no details of the technique used to measure the line intensities. For measurements that depended on knowledge of effective neutron capture cross sections for computing absolute capture-gamma-ray intensities, the cross-section values used are footnoted to the tables if they were supplied by the author in his paper. Unfortunately, these cross sections are often not present.

Two groups, that of Kinsey and Bartholomew[11–13] and that led by Groshev,[14] have accounted for a significant fraction of the total measurements of thermal-neutron capture-gamma-ray spectrums made to date. The techniques they used to measure capture-gamma-ray intensities are discussed in some detail in the report text.

Atlas Format

The four thermal-neutron capture-gamma-ray spectrums generally measured for each element are low-energy spectrums measured with the 1.5- by 1-in. and with the 3- by 3-in. NaI(Tl) scintillation detector and high-energy spectrums measured with the 3- by 3-in. and with the 5- by 4-in. NaI(Tl) scintillation detector. For a specific element X, these four spectrums are designated as $(X-1)$, $(X-2)$, $(X-3)$, and $(X-4)$, respectively. When more than one spectrum of a particular type is measured, for instance, two low-energy spectrums measured with different energy ranges using the 3- by 3-in. NaI(Tl) crystal, they are designated as $(X-2)$ and $(X-2a)$. In addition, a box at the upper right-hand corner of the figure gives the NaI(Tl) crystal size, the chemical form of the sample, the total mass of the sample (excluding the aluminum-foil container), the "true" sub-cadmium neutron flux measured at the sample position, and the live counting time used to obtain each of the four spectrums required for use in Eq. 1.

The four thermal-neutron capture-gamma-ray spectrums obtained for each element are contained as an integral part of a short section which discusses the thermal-neutron capture-gamma-ray spectral structure of that element. In addition, each element section contains subsections on (1) thermal-neutron reactions and (2) effective capture cross sections, as well as (3) references to prior studies of the neutron capture-gamma-ray spectrums of the element and (4) tables containing both the low- and high-energy capture-gamma-ray energies and intensities measured in this present work and by prior investigators. Inclusion of the detailed capture-gamma-ray cross-section information with each section should allow intensity values determined from the present spectrums to be corrected quite easily if more accurate cross-section measurements become available. (R. E. Greene)

(References for this article are on page 358, following the appendix.)

ISOTOPES AND RADIATION TECHNOLOGY, Vol. 4, No. 4, Summer 1967

Appendix

SAMPLE PAGES FROM THE ATLAS OF THERMAL-NEUTRON CAPTURE-GAMMA RAYS

Atlas of Thermal-Neutron Capture-Gamma Rays

IRON

Thermal Neutron Reactions

$$Fe^{54}(5.82\%)(n,\gamma)Fe^{55}(\sigma = 2.9b) \xrightarrow[EC]{2.7y} Mn^{55}(\text{Stable})$$

$$Fe^{56}(91.66\%)(n,\gamma)Fe^{57}(\sigma = 2.7b)\ (\text{Stable})$$

$$Fe^{57}(2.19\%)(n,\gamma)Fe^{58}(\sigma = 2.5b)\ (\text{Stable})$$

$$Fe^{58}(0.3\%)(n,\gamma)Fe^{59}(\sigma = 1.1b) \xrightarrow[\beta^-]{49d} Co^{59}(\text{Stable})$$

Effective Capture Cross Section

$$\sigma_c\ (2200) = (2.62 \pm 0.06)b^{27}$$

and $g = 1.000$ and $[s]_{\mu kT}^{0.45} = 0$

thus $\hat{\sigma}_c = (2.62 \pm 0.06)b$

Comments

The Fe^{56} isotope accounts for approximately 91 percent of all the thermal neutron capture reactions in natural iron. Consequently, the great majority of the lines which have been observed in the neutron capture gamma ray spectra from natural

iron result from gamma ray transitions in Fe^{57}. The weak

cently, Bartholomew and Vervier[68] have made angular correla-

iron result from gamma ray transitions in Fe^{57}. The weak 416 keV line which is observed in (Fe-2) and (Fe-2a) is however most probably interpreted as due to prompt gamma radiation emitted in transitions from the first excited state of Fe^{55} to the ground state. With this interpretation, the intensity of the 416 keV ground state transition in Fe^{55} would be about 30 percent. In addition, the 813 keV line can tentatively be assigned as due to capture gamma rays emitted in transitions from the first excited state of Fe^{58} to the ground state. Again, with this interpretation, the intensity of the 813 keV ground state transition in Fe^{58} would be about 67 percent.

Comparison of the absolute intensities measured in this present work for the 1628 keV and 1730 keV capture gamma rays to those reported by Groshev et al.[129] in a very recent paper, shows excellent agreement. The gamma ray energy and intensity values reported by Groshev et al.[129] in this recent work can be considered to supersede those reported earlier by Adyasevich et al.[76] since both papers are authored by the same group.

Measurements of the low energy thermal neutron capture gamma ray spectra of iron have also been reported by Urbanec et al.[105] Many of the lines observed by Urbanec et al.[105], and interpreted by them as being iron neutron capture gamma ray lines, are not observed in either the present spectra, or by Fiebiger et al.[130] Comparison of these three separate sets of spectra shows that the low energy iron neutron capture gamma ray spectrum measured by Fiebiger et al.[130] is essentially identical to (Fe-2a), while the spectrum obtained by Urbanec et al.[105] is much inferior to these, showing predominantly an iodine neutron capture gamma ray structure. Consequently, the very strong 851 keV line, and the weaker 442 keV 316 keV and 152 keV lines observed by Urbanec et al.[105] cannot be interpreted as due to iron neutron capture gamma rays. Similarly, the 454 keV and 313 keV lines observed by Adyasevich et al.[76] are not observed in either the present work or by Fiebiger et al.[130]

Comments

There have been numerous studies of the prompt gamma rays emitted as a result of neutron capture in iron. Hamermesh and Hummel[5] provided one of the first measurements of the iron neutron capture gamma ray spectrum while more re-

cently, Bartholomew and Vervier[68] have made angular correlation measurements on the iron neutron capture gamma ray cascades, Carlos et al.[128] have studied the two step gamma-gamma cascades between the capturing state and the ground state in Fe^{57} using sum coincidence circuitry with two NaI(Tl) scintillation detectors, and Trumpy[83] and Vervier[84] have measured the circular polarization of the 7.63 MeV prompt gamma rays which result from the capture of polarized neutrons by Fe^{56}. In addition, Moore et al.[131], Wasson and Draper[110], and Block[132] have measured the prompt gamma rays spectra which result from resonance neutron capture in iron. Finally, Ewan and Tavendale[133] and Slaughter and Harvey[134] have measured the neutron capture gamma ray spectrum of iron with the recently developed lithium drifted germanium gamma ray detectors to allow resolution of the 7639 keV and 7625 keV prompt gamma ray lines resulting from transitions from the capturing state of Fe^{57} to the ground state and first excited state, respectively.

Table Fe-I
LOW ENERGY THERMAL NEUTRON CAPTURE GAMMA RAYS FROM IRON

Present Work		Groshev et al.[129]		Adyasevich et al.[76]		Fiebiger et al.[130]	Reier and Shamos[115]
E_γ, keV	I_γ	E_γ, keV	I_γ	E_γ, MeV	I_γ	E_γ, keV	E_γ, MeV
124	3.0					118	
160(M)	1.9						
231(M)	2.7					226	
286(M)	1.4						
				0.313	3.2		
356(M)	15.4			0.364	6.2	353	0.355
416	1.9						
				0.454	4.1		
514(M) (A+γ)	11.8					514(M) (A+530)	
590	1.1						
697(M)	8.1					698	
813	1.4					821	
906(M)	4.5					916	
1026	2.5					1028	
1265	6.1	1264	4	1.236	1.5	1274	
				1.530	1.9		
1628(M)	9.6	1613	10	1.626	6.1	1628	1.55
1730	9.5	1727	11	1.72	6.4	1722	1.68
				1.80	2.3		
		2070	0.7				
2140(M)	3.5	2138	0.8	2.143	1.4		

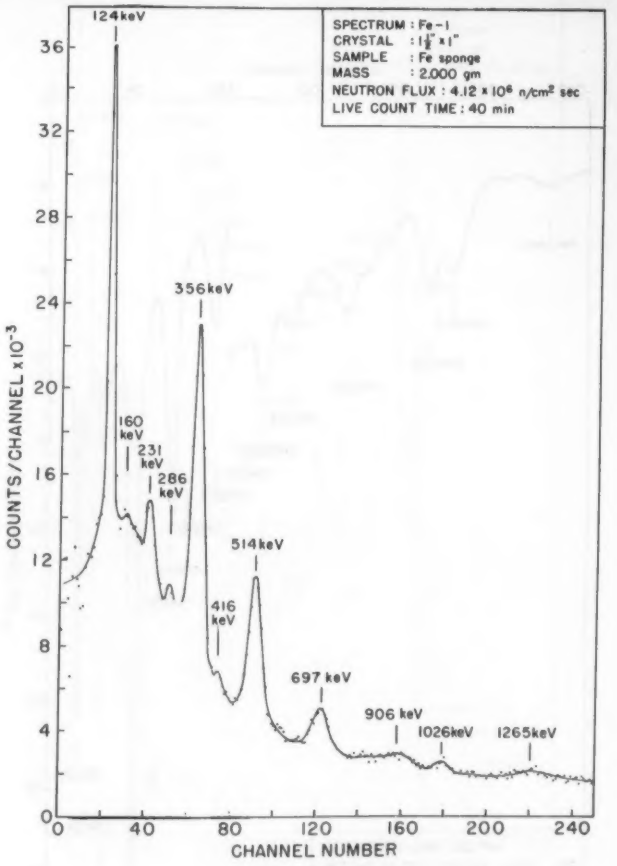
Table Fe-II
HIGH ENERGY THERMAL NEUTRON CAPTURE GAMMA RAYS FROM IRON

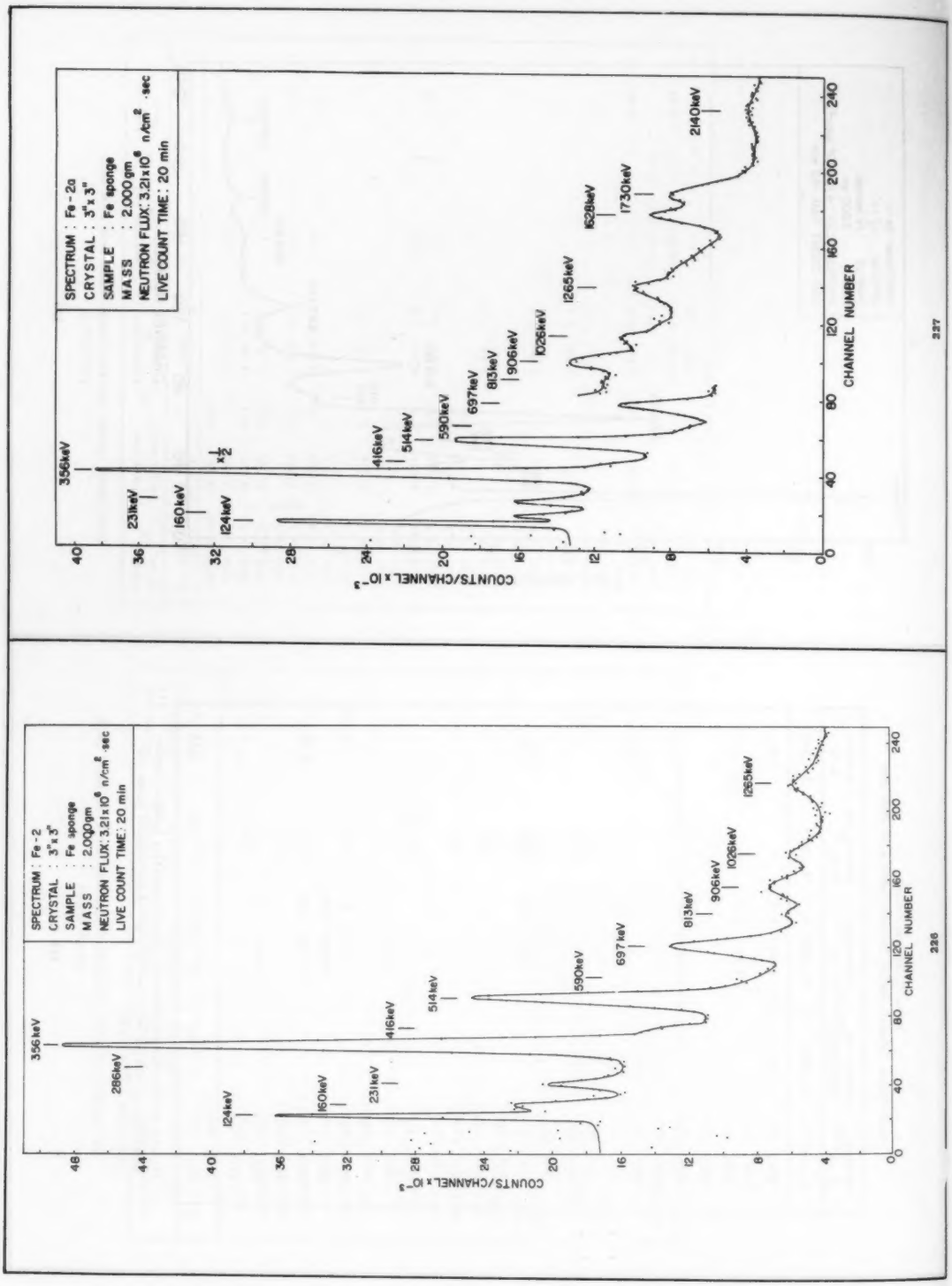
Groshev et al.[129]		Kinsey and Bartholomew[2,122]		Adyasevich et al.[76]		Bostrom and Draper[51]	Present Work	
E_γ, keV	I_γ	E_γ, MeV	I_γ^*	E_γ, MeV	I_γ	E_γ, MeV	E_γ, MeV	I_γ
10038	0.03	10.16	0.06					
9298	3.3	9.298	2	9.295	2.7	9.295	9.30	
8882	0.5	8.872	0.3	8.86	0.3			
8368	0.3	8.345	0.6	8.34	0.2			
7643	21.5	7.639	21	7.636	31.5	7.64	7.64	62
7629	21.5							
7277	5.3	7.285	3	7.275	5.3	7.28	7.63	
6831	0.07							
6504	0.1							
6379	0.6	6.369	0.3	6.43	0.7			
6295	0.1							
6269	0.1							
6018	8.5	6.015	6	6.026	7.9	6.03	5.97	
5920	8.3	5.914	6	5.92	8.7	5.92		
5787	0.2							
5750	0.2							
5499	0.2			5.51	0.6			
5046	0.2							
5013	0.2							
4950	0.8	4.968	0.6	4.94	0.9			
4885	0.1							
4810	1.9	4.81	1	4.805	2.1			
4680	0.3							
4662	0.1							
4462	0.5	4.44	1	4.405	2.2		4.42	
4405	1.4							
4274	0.4							
4217	3.3	4.21	2	4.220	4.3	4.22	4.23	
4014	0.4			4.03	1.4			

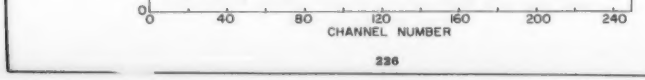
Table Fe-II (continued)
HIGH ENERGY THERMAL NEUTRON CAPTURE GAMMA RAYS FROM IRON

Groshev et al.[129]		Kinsey and Bartholomew[2,122]		Adyasevich et al.[76]		Bostrom and Draper[51]	Present Work
E_γ, keV	I_γ	E_γ, MeV	I_γ^*	E_γ, MeV	I_γ	E_γ, MeV	E_γ, MeV
3855	1.2	3.86	0.7	3.844	2.3		3.85
3792	0.3			3.72	1.1		
3778	0.3						
3665	0.2						
3504	0.3			3.55	1.4		
3489	0.6						
3440	2.2	3.43	2	3.430	3.9	3.43	3.42
3416	2.5						
3360	0.5						
3325	0.1						
3296	0.5						
3276	1.7			3.240	2.9	3.24	3.22
3242	0.4						
3228	1.0						
3192	1.0						
3172	0.6			3.15	2.1		
3109	0.7						
3068	0.5						
2955	0.7						
2880	0.5						
2836	0.8			2.840	2.1		
2720	2.1			2.730	2.9	2.73	2.73
2698	0.5						
2683	0.5			2.67	1		
2535	0.6						
2476	0.5						
							2.42

*Kinsey and Bartholomew obtained these intensities using an intercomparison technique with the 8.53 MeV nickel capture gamma ray line; with a $\bar{\sigma}_\gamma$ = 2.43b.




SPECTRUM : Fe-2a
CRYSTAL : 3"x3"
SAMPLE : Fe sponge
MASS : 2.000 gm
NEUTRON FLUX: 3.21x10⁶ n/cm² ·sec
LIVE COUNT TIME: 20 min
356keV
231keV
160keV
124keV
x1/2
416keV
514keV
590keV
697keV
813keV
906keV
1026keV
1265keV
1529keV
1730keV
2140keV
COUNTS/CHANNEL x 10⁻³
CHANNEL NUMBER
227
SPECTRUM : Fe-2
CRYSTAL : 3"x3"
SAMPLE : Fe sponge
MASS : 2.000gm
NEUTRON FLUX: 3.21x10⁶ n/cm² ·sec
LIVE COUNT TIME: 20 min
356keV
286keV
124keV
160keV
231keV
416keV
514keV
590keV
697keV
813keV
906keV
1026keV
1265keV
COUNTS/CHANNEL x 10⁻³
CHANNEL NUMBER
226



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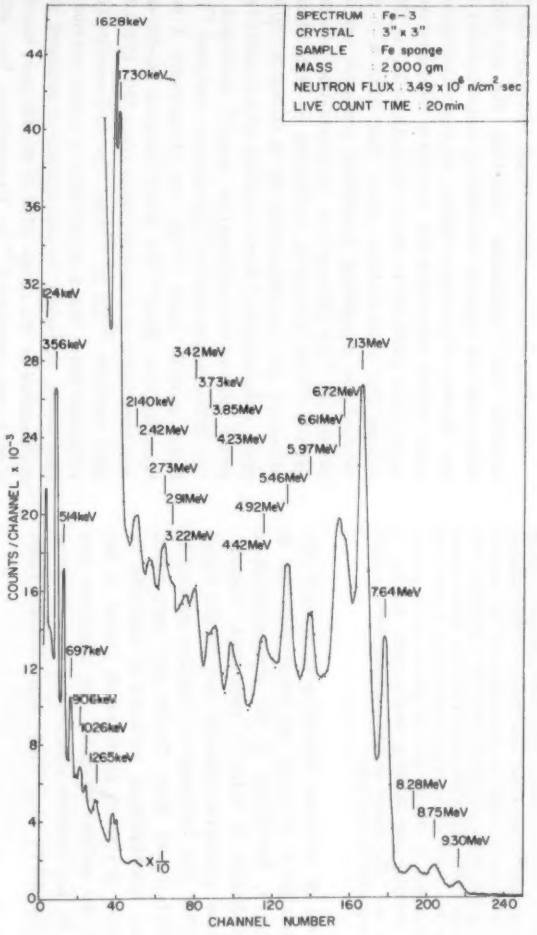

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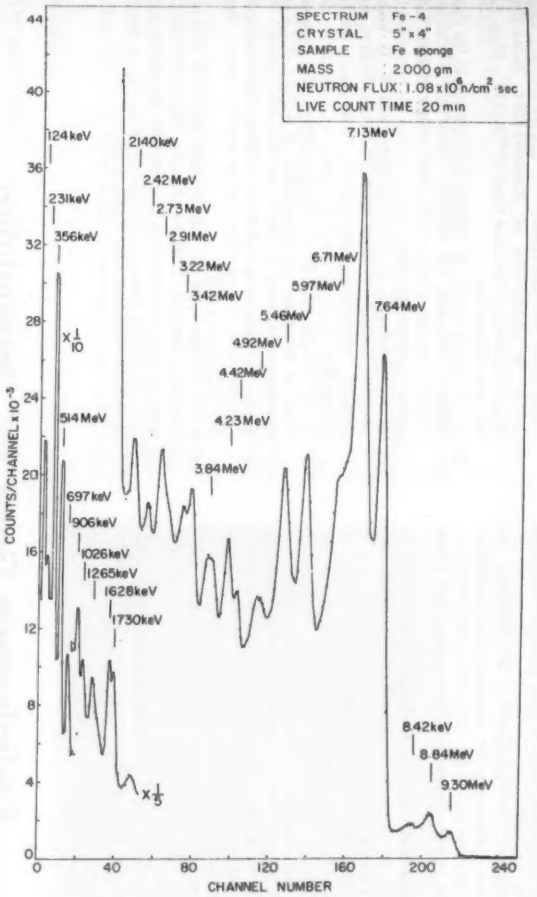

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Radioisotope Gage for Determining Suspended-Sediment Concentration in Streams*

Abstract: An internally powered self-referencing gage was developed for determining suspended-sediment concentrations in water of 1000 to 50,000 ppm to an accuracy better than ±20%. The measuring head, containing a ^{109}Cd source, is mounted under water, and the attenuation of the emitted X radiation by the sediment-laden water is compared with that by distilled water. Data are recorded by a shore-based unit. The source must be replaced about once a year. Its activity is such that no special procedures or markings are required in shipping and handling and no AEC license is required for use. The major system components are light enough to be carried by one man.

In the control of sediment deposition to prevent filling up of navigable streams and reservoirs and in erosion studies, knowledge of the concentration of suspended sediment in water is important. Concentrations to be measured usually fall in the range 1000 to 50,000 ppm, although in regions subject to seasonal rainfall and flash floods they may reach 200,000 ppm. Conventional methods of analysis, in which samples are taken at different places in the stream and the solids weighed, are laborious and slow. They do not monitor short-term concentration excursions, cannot be used where unpredictable flash floods occur, and do not truly represent flowing-stream conditions.

Advantages of the radioisotope technique are the capacity for continuous sampling, the low power drain, and the capacity for making measurements under flowing-stream conditions. An early radioisotope gage, which measured the density of deposited sediment, was patented by Hitch, Bizzell, et al.[1] in 1955. Among the radioisotope gages that have been developed for measuring suspended sediment was one based on ^{60}Co gamma-ray transmission.[2] Another used a ^{170}Tm source in scattering or transmission geometry for concentrations up to 60,000 or 500,000 ppm, respectively.[3] Early models of a portable two-probe gamma-ray-attenuation gage[4,5] developed by the USDA Sedimentation Laboratory contained ^{137}Cs; later models used ^{109}Cd. An inexpensive X-ray-transmission gage[4,5] for short-duration on-the-spot measurements of concentrations from 5000 to 300,000 ppm contains ^{109}Cd or ^{241}Am. The radioisotope gage reviewed here, which is intended to make continuous, long-term, accurate measurements of sediment concentrations in the range 1000 to 50,000 ppm, was designed and developed[4-6] by Parametrics, Inc., under the sponsorship of the Division of Isotopes Development, USAEC, and is now being field-tested[7] with the cooperation of the Federal Interagency Sedimentation Project. Early work on the gage was described

*J. Roger McHenry of the USDA Agricultural Research Service, Soil and Water Conservation Research Division, Oxford, Miss., and Bach Sellers of Parametrics, Inc., Waltham, Mass., kindly criticized this review before publication.

briefly in a previous issue of this review.[8] The results of the field tests will be reported later.

Gage Description

SPECIFICATIONS

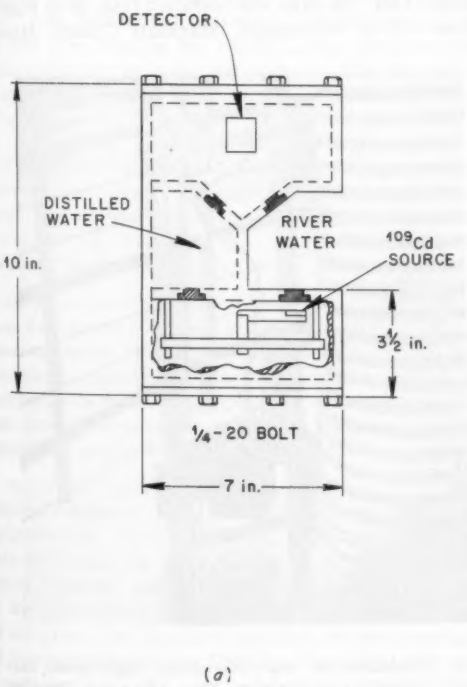
The original specifications for the self-referencing single-probe gage were

1. Operation over a concentration range of 1000 to 50,000 ppm of sediment of average density of 2.65 g/cm^3
2. Accuracy of ±20% at 1000 ppm by weight (better at higher concentrations)
3. Data record on a strip chart at 15-min intervals
4. Service period (battery recharge, etc.) of 7.5 days
5. Operating temperature of 32 to 85°F for measuring head and of 20 to 120°F for shore station
6. Operation by four lead–acid batteries of 100 amp-hr capacity each, nominal 12 volts (later adapted to use 115-volt alternating current when available)

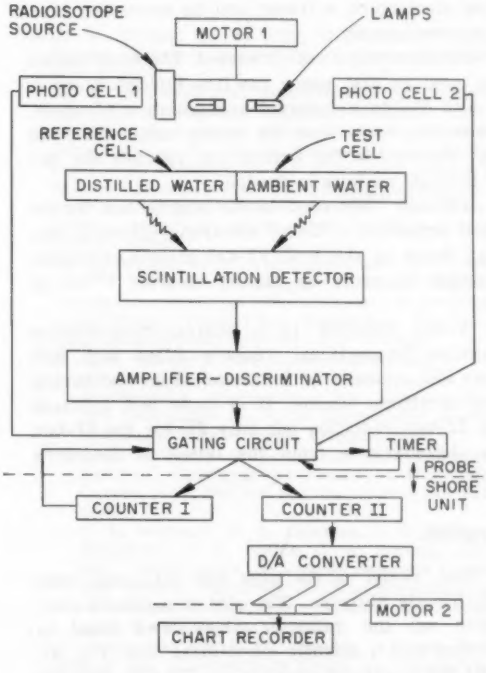
OPERATION

The gage (Fig. 1) operates by alternately measuring the transmissions of X radiation through water containing suspended sediment (river water) and through distilled water (Fig. 2*a*) and then comparing beam intensities. If no appreciable amount of dissolved material is present, the ratio of the two values is a function of the suspended-sediment concentra-

Fig. 1 Components of the self-referencing, single-probe, suspended-sediment-concentration gage (early model).



(*a*)



(*b*)

Fig. 2 (a) Measuring head and (b) schematic installation of self-referencing, single-probe, suspended-sediment-concentration gage (early model).

tion. Since a ratio rather than an absolute value is recorded, errors due to source decay and to changes in the X-ray detector response, the electronics, and the liquid density are eliminated.

When the gage is operating, the source is mechanically switched every 12 sec so that the beam passes alternately between a sealed cell containing distilled water and an open one through which river water is flowing. The radiation that passes through reaches a detector, and data from the detector are transmitted to recording equipment (Fig. 2*b*).

The source must be replaced at approximately yearly intervals. This is a simple mechanical operation that can be performed in the field by trained personnel.

CONSTRUCTION

The parts to the gage—the submersible head and the weatherproof shore-based unit—are connected by 50 ft of flexible waterproof cable.

The brass measuring head, which weighs 50 lb and is 7.5 by 9.5 by 11 in., contains the radioactive source, the distilled-water and river-water cells, a mechanism for switching the source between them, and the X-ray detector, preamplifier, and high-voltage supply. The 17-lb shore unit is an aluminum box, 16 by 9 by 8 in., containing a digital printer, the counting electronics, a timer, and the necessary low-voltage power supply.

The distilled-water cell is sealed. The river-water cell is open so that water can flow through it and is lined with Teflon to prevent accumulation of algae. The radiation beam from the source enters the cells through windows in the bottom and reaches the detector through windows in the top.

The 453-day ^{109}Cd used in the source has for its principal emission a 22-kev electron-capture X ray, although there is also a 4% 87-kev gamma emission. The source is made by plating metallic ^{109}Cd on copper.

The X-ray detector is a square-cross-section side-window proportional counter filled with 90% krypton–10% methane at 2 atm pressure and having a 5-mil beryllium window. It is about 80% efficient for the 22-kev radiation but only 2% for the 87-kev gamma. Interference from the latter is therefore low.

Calibration

The final model of the gage was calibrated with montmorillonite slurries. The plot of sediment concentration vs. the ratio of observed count to water count was a slightly curvilinear line (Fig. 3), which fit the empirical equation $x = 739{,}000 - 369{,}500 \times (\log 100y)$, where x is the total solids concentration in the water and y is the ratio of observed counts to counts of the water standard.

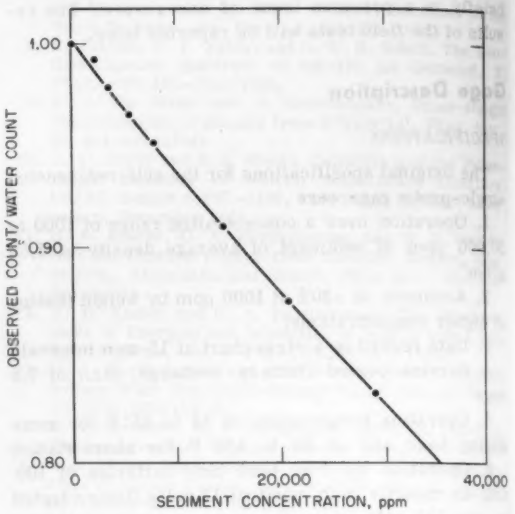


Fig. 3 Calibration curve for sediment-concentration gage made with montmorillonite suspensions.

Field Tests

For a preliminary field test[6] in February and March 1966, the gage was installed (Fig. 4) in Pigeon Roost Creek Watershed, Marshall County, Miss.,

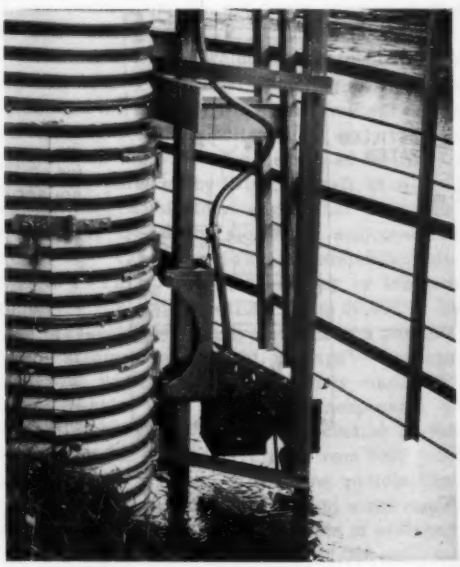


Fig. 4 Installation of self-referencing, single-probe, suspended-sediment-concentration gage showing traveling dolly with detector head attached. Note the signal cable, which is loosely attached to the steel cable holding the dolly.

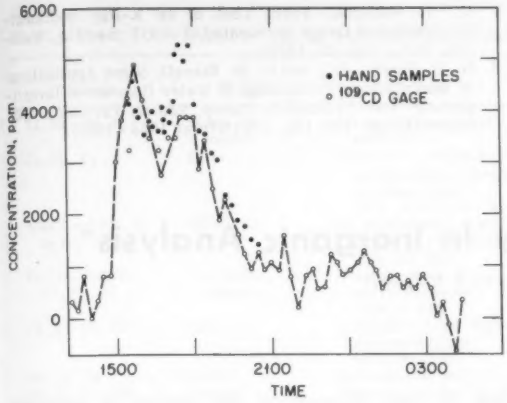


Fig. 5 Sediment concentration in runoff from storm of Mar. 3–4, 1966. Negative concentrations indicate readings lower than laboratory standard, in this case tap water whose dissolved-solids content was comparable to that of the creek at base flow.

which drains a 50-sq mile area. The channel at the point of installation is 70 ft wide, the water flow is continuous at 8 to 10 second-feet (cfs), and the mean solids concentration is 5 to 20 ppm. Three storms occurred during the two months' installation, and, during flood runoff, peak flow rates were 6720 sec-ft and peak suspended-sediment concentrations were 15,000 ppm. During the runoff period samples were also collected by hand and analyzed. The concentrations found by the two methods were in agreement (Fig. 5).

The results of the test were definitely promising. Several components were not up to design specifications, but the next model should be capable of greater accuracy and reliability. The degree to which specifications were met is shown by the following:

Concentration. The practical lower limit of detection was about 500 ppm, and errors associated with measurements of concentrations less than 1000 ppm increased rapidly as the concentration decreased. Response at the higher specified concentrations was not tested because the maximum concentration encountered in this test was 15,000 ppm.

Accuracy. With a ±20% sensitivity at 1000 ppm, concentrations of 1000 and 1400 ppm should be distinguishable. The calibration curve indicates that this difference is equivalent to about 5 units on the chart readout, and this is statistically significant if the unit is functioning properly and the data spread is not great. The standard deviation for the responses at concentrations below 1000 ppm was about 200 ppm.

Readout. With the readout mechanism set for 15-min intervals, some 40 min is lost during a 24-hr period. For routine use, a 3-min correction was necessary every 2 hr so that readout time would coincide with clock time.

Service Period. The unit functioned up to 5 days with no battery servicing. However, because of the differential battery drain, it was thought desirable to recharge the batteries more frequently than once a week. The timer motor in the shore unit failed after 237 hr of operation.

Operating Temperature. The measuring head performed within specifications, but the shore station was not temperature stable between 20 and 120° F.

Power. The use of four lead–acid batteries tapped at differing voltages led to differential discharge of the battery cells, and rapid battery recharge was difficult. This is a serious operating problem and should be eliminated by the use of a voltage divider in the shore unit to permit the use of the full 12 volts from the storage batteries.

Large-scale field tests in a number of locations throughout the United States are now under way with an improved model. Not enough data have been obtained to indicate trends in the gage operation, but early reports are favorable. (Martha Gerrard)

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Thin-Layer Chromatography in Inorganic Analysis*

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[Editor's Note: Thin-layer chromatography is a potentially very useful technique for separating radioisotopes for either analytical or preparative purposes. A translation of a recent Russian review is given below to illustrate the wide application of this technique. The use of thin-layer chromatography in radioassay was reviewed by Fred Snyder of the Oak Ridge Institute of Nuclear Studies in *Atomlight*, No. 58 (February 1967)(15 pp., 67 references).]

Abstract: The literature on inorganic thin-layer chromatography (83 references) since 1960 is reviewed. The survey indicates that this technique could be used more extensively than it is now for inorganic analysis and is especially valuable for handling of micro amounts of material and for performing basic theoretical studies.

Thin-layer chromatography (TLC) has been widely used in organic chemistry. Because of its sensitivity it is an excellent method for separating and concentrating small amounts of substances from complex mixtures. It is applicable under a wide variety of conditions and is both simple and rapid in operation. The principles of the technique, the technology, and the experimental procedures together with examples of application to the solution of analytical problems have been given in various reviews and theoretical papers.[1-21]

Briefly, the ascending TLC method consists of the following steps: A thin layer of about 200-mesh sorbent (250 to 200 μ) is spread on a glass plate, with or without gypsum or starch binder. A small volume (0.001 to 0.003 ml) of the solution being studied is placed by means of a capillary at the edge of the sorbent layer, which is about 1.5 cm from the edge of the plate, as is done in paper chromatography. The plate is then placed in a chamber saturated with solvent vapor so that the layer being tested extends about 0.5 cm into the liquid solvent.

The location of the zones of the separated components depends on the value of a parameter, R_f; this in turn depends on the method of operation (ascending, descending, or horizontal chromatography), the thickness and efficiency of the sorbent, the amount of solvent used and its path length, and the relative amounts of the elements in the solution under study. Therefore the value of R_f cannot be readily calculated, and, in addition to the unknown solution, drops of known solutions of elements are used as "blanks."

The physical and chemical properties of the individual ions are used to show the corresponding zones. A good method for bringing out the zones is to spray the chromatogram with reagents that react with the elements being studied to give color or fluorescence. Sometimes radioactive isotopes are used. If the TLC method is combined with sensitive instrumental methods, such as mass spectroscopy,[22] infrared spectroscopy,[23] or radiochemistry,[24,25] very small amounts of substances can be definitely and individually identified.

Since TLC has been used in inorganic chemistry for only about 5 years, only a few papers have been published in this field.[26-55] Examples of its use are shown in Table 1. The method rapidly separates and clearly identifies amounts of inorganic substances as small as 10^{-6} to 10^{-7} mole, i.e., from tenths or even hundredths of a microgram to some tens of micrograms. The separation time is usually no more than 30 to 90 min. For these reasons TLC offers good possibilities for studying very small amounts of materials when other methods of chemical analysis are not suitable.

The TLC method also gives very good results in the separation of (1) very similar elements, e.g., sodium and potassium;[24] calcium, strontium, and barium;[30] iron, nickel, and cobalt;[32] rare-earth elements;[40,41] selenium and tellurium;[43] (2) the different valence states of a single element, e.g., Cr(III) and Cr(VI);[27] As(III) and As(V); Sb(III) and Sb(V); or Hg(I) and Hg(II).[26]

By judicious choice of the sorbent, the method of operation (ascending or descending chromatography either with binder or without binder), and the method

*Edited version of Part I. Possibilities of Inorganic Thin-Layer Chromatography. A Review, *Zhurnal Analiticheskoi Khimii*, 21(11): 1348-1352 (1966)(in Russian), English translation ORNL-tr-1603 by Martha Gerrard).

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Table 1 USE OF THIN-LAYER CHROMATOGRAPHY FOR SEPARATING INORGANIC IONS

Mixture	Sorbent	Solvent	Detection reagent	Sensitivity, *M*, for each element	Separation time	Reference
Li, Mg, Na, K	Silica gel, starch	Ethanol–glacial acetic acid (100 : 1)	Violuric acid	1×10^{-6}	50–70 min	39
Ca, Sr, Ba	Ditto	Ethanol–*n*-propanol–glacial acetic–acetyl acetone–water (37.5 : 37.5 : 5 : 1 : 20)	Ditto	1×10^{-6}	80–90 min	30
Alkali metals, alkaline earths	Silica gel	5% ethanol soln. glacial acetic or 5% butanol soln. 2*M* HCl	Violuric acid or tetracyanoquinodimethanide	2×10^{-6}–5×10^{-5}	1–2 hr	31
Fe, Zn, Co, Mn, Cr, Ni, Al	Silica gel, gypsum	Acetone–conc. HCl–acetonylacetone (100 : 1 : 0.5)	8-Hydroxyquinoline in uv. light	2×10^{-7}	15–20 min	32
Hg, Bi, Cd, Pb, Cu	Ditto	*n*-Butanol–1.5*M* HCl–acetonylacetone (100 : 20 : 0.5)	KI, H_2S	2×10^{-7}	2 hr	32
Pb, Ag, Hg	Starch	Acetone–3*M* HNO_3 (1 : 1)	$(NH_4)_2S$	1×10^{-8}–5×10^{-9} g-eq	2 hr	33
Ba, Sr, Ca, Mg	Starch	Acetone–3*M* HCl (2 : 3)	8-Hydroxyquinoline in uv. light	1×10^{-8}–5×10^{-9} g-eq	2 hr	33
Hg, Pb, Bi, Cu, Cd	Starch	Acetone–3*M* HCl (1 : 1)	$(NH_4)_2S$	5×10^{-8}–5×10^{-9} g-eq	2 hr	34
As, Sb, Sn	Starch	Ditto	Dithizone in $CHCl_3$	5×10^{-8}–5×10^{-6} g-eq	2 hr	34
Hg, Bi, Sb, Cd, As, Pb, Cu, Tl	Kieselguhr	Acetone–benzene (3 : 1) satd. with tartaric acid, 10% HNO_3	Dithizone or $(NH_4)_2S$		3 hr	35
UO_2^{2+}	Silica gel, gypsum	Ethyl acetate–diethyl ether–TBP (50 : 50 : 2)	Pyridyl azonaphthol in C_2H_5OH	1 μg U	10–15 min	37
Ga	Ditto	Acetone–conc. HCl (100 : 0.5)	8-Hydroxyquinoline in uv. light	1 μg	-	37
Au, (Os, Ru), (Pd, Pt), (Rh, Ir)	Ditto	Acetone–conc. HCl–aceto-acetic ester (100 : 1 : 100)	-	-	20–25 min	38
Au, (Os, Pt, Ru, Pd, Ir), Rh	Ditto	Ditto (25 : 15 : 25)	-	-	-	38
Au, Pt, Pd	Silica gel, gypsum	*n*-Butanol–conc. H_2SO_4–H_2O (100 : 2.5 : 97.5 or 100 : 5 : 95)	-	-	90 min	38
Ag, Au, Pd, Pt	Kieselguhr	Benzene–CH_2Cl_2 (1 : 1)	Natural dithizonate color	-	-	39
La, Pr, Sm	PVC–PVA* copolymer impregnated with di(2-ethylhexyl) phosphoric acid	0.25–0.9*M* HCl (horizontal chromatography)	8-Hydroxyquinoline or radioisotopes	-	10 min	40
Tb, Gd, Er	Ditto	Ditto	Ditto	-	10 min	40
Tb, Eu, Nd	Ditto	Ditto	Ditto	-	10 min	40
Rare earths	Silica gel, starch	1*M* di(2-ethylhexyl) phosphoric acid in CCl_4	Radioisotopes	-	-	41
Ti, Zr, Th, Sc, Nb, U	Silica gel	TBP–benzene (3 : 7)	-	-	-	42
U	Silica gel	*n*-Butanol–acetyl-acetone–acetic acid	-	-		42
Se, Te	Ditto	TBP–benzene satd. with conc. HCl or thiourea–6*M* HCl	-	-	2 hr	43
F, Cl, Br, I	Silica gel, gypsum	Acetone–*n*-butanol–conc. NH_3–H_2O (65 : 20 : 10 : 5)	Ammonia–alkali soln. $AgNO_3$, uv. fluorescence; Zr–alizarin lake	1×10^{-6}	30–40 min	46
I, Br, Cl, PO_4^{3-}	Silica gel, $AgNO_3$	H_2O satd. with isobutanol–4% CH_3COONH_4 (4 : 1)	-	-	-	46
Phosphates	Silica gel, starch	CH_3OH–conc. NH_4OH–10% CCl_3COOH–H_2O (50 : 15 : 5 : 30)	$(NH_4)_2MoO_4$, $SnCl_2$ in 10% HCl	-	50–60 min	48
Sulfates and polythionates	Silica gel starch	CH_3OH–propanol–conc. NH_4OH–H_2O (50 : 50 : 5 : 10) or CH_3OH–dioxane–conc. NH_4OH–H_2O (30 : 60 : 10 : 10)	Ammonia soln. $AgNO_3$, bromcresol green	-	45 min	50

*Polyvinyl chloride–polyvinyl acetate.

of chromatography (absorption, distribution, or ion exchange) and adaptation of techniques used in other analytical methods (e.g., superposition of an electric field or precipitation), wide possibilities are opened up for using TLC in inorganic analysis. Most of the published methods for separating inorganic ions use a sorbent with a binder, e.g., silica gel with gypsum or starch, and ascending chromatography.

Besides silica gel it is possible to use aluminum oxide, cellulose, ion-exchange resins, or Sephadex. Ion-exchange resins have been used to separate halogens (Dowex 1)[56] and iron, nickel, and cobalt (Dowex 50),[57] and inorganic ion exchangers (zirconium phosphate and hydroxide) have been used to separate alkali and alkaline-earth elements.[58]

A very good method for increasing the efficiency of the TLC method is to combine it with electrophoresis,[59–63] in which case the separation requires only 2 to 3 min with high voltages and up to 1 hr with low voltages. Precipitation TLC is also very efficient;[64] for example, a mixture of iodide, bromide, and chloride ions is readily separated by precipitation chromatography on a layer of silica gel impregnated with silver nitrate. The halides are separated according to the difference in solubility of the precipitates formed, the zones from the edge inward being AgI, then AgBr, and finally AgCl. In sunlight the zones are colored yellow, gray, and gray-violet, respectively.

The components of complex mixtures may be separated by multidimensional TLC, e.g., mono-, di-, and triphosphoric acids by two-dimensional chromatography.[65]

The TLC method is also used as a preparative technique,[66–71] i.e., for separating milligram amounts of mixtures and for obtaining pure materials (e.g., sample preparation). In this case the plate size and sorbent-layer thickness are increased. It is convenient to use sorbent (aluminum oxide or silica gel) without binder on plates up to 40 cm wide and 80 cm long and sorbent-layer thicknesses of 1.5 to 3 mm with 20 to 25 mg of sorbent per centimeter of distance from the edge.[71] For obtaining pure substances the sorbent and solvent must be carefully purified.

The TLC method also has possibilities for control of purification processes because of the rapidity with which the purity of intermediate products can be checked. Fractions obtained by column chromatography may be rapidly analyzed, either directly on the chromatogram or in the eluate.[72–78] In the first case, depending on the size of the spots, quantitative analysis or photometry is used; in the second, spectrophotometric, luminescent, or polarographic methods are appropriate.

A few papers have been published[78–83] on such diverse phases of the subject as nature of the sorption mechanism, effect of formation of complexes between various cations and solvents, hydration and hydrolysis of complexes, effect of the sorption isotherm form and the concentration of substances in the spots on the value of R_f, and the relation between the weight of a substance in a spot and its area. (MG)

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Potential Markets for Radioisotope-Based Analytical Equipment*

Abstract: A survey of French metallurgical, chemical, and mining industries, sponsored by the Commissariat à l'Energie Atomique, indicated that analytical techniques based on radioisotope-generated X-ray fluorescence in particular but also on gamma-radiation absorption and beta-radiation backscattering could, in many cases, profitably replace or complement standard physical and chemical methods of analysis. Equipment for continuous analysis and process control is of interest, and the time appears ripe for rapid development of industrial radioisotope-based equipment.

The characteristic X ray emitted ("fluoresced") by an element that is being bombarded by photons or charged particles may be used to determine that element in a system. The increasing importance of the "X-ray fluorescence" technique, as it is called, is indicated by the fact that two international conferences have been held in this field.[1,2] Satisfactory methods for process-stream analysis and process control have been developed in which the characteristic X ray generated by photons from a radioisotope source, absorption of a radioisotope gamma emission, or backscattering of a radioisotope beta emission are used. However, the effort in general has been to solve specific problems rather than to design general equipment that can be adapted to specific cases. Several fields of industry — metallurgy, industrial chemicals, and mining — were therefore surveyed to determine whether or not a more general application is feasible.

Although good equipment is available for the standard analytical methods now in use — emission and absorption spectrometry, gravimetric and colorimetric methods, and X-ray fluorescence with an X-ray machine — some of the methods are destructive and equipment is usually not portable. Considerable time may elapse after the sample has been taken before the results are obtained, and continuous analysis is often not practicable.

Equipment based on radioisotopes, on the other hand, lends itself well to plant application. It is sturdy, easily handled, low in operating cost, and portable. Minimum sample preparation is required, analytical results are obtained immediately, and the methods are nondestructive and readily adaptable to continuous analysis.

Not many applications to continuous analysis were found during this survey, but those which were encountered are very important industrially. Firms interested in this type of analysis generally want immediate results, and in most cases they visualize eventual automatic regulation. Only the largest firms

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showed an interest in this application, but they will consider higher installation costs provided the system can show economy in material or labor, increase in production, or improvement in quality.

Organization of Survey

Firms were selected to participate in the survey on the basis of the economic importance of the branch of industry represented, the standing of the firm, the nature of its products, and its interest in new methods. Visits were made to 44 firms, and questionnaires were sent to 52 others. Industrial cooperation was good, with 41 of the 44 firms visited indicating interest and 50% of the firms returning the questionnaires. Understandably, results of the visits were much more useful than those of the questionnaires. In the absence of a trained surveyor to orient the discussions, the recipients considered only the unsolved problems, not the possibilities of installing radioisotope techniques to replace analytical procedures already in use.

As a part of the survey, a brochure describing the principles of X-ray-fluorescence, gamma-absorption, and beta-backscattering analytical methods and results already achieved with them was sent to each firm. The brochure was very important in the success of the visits. However, those who received the questionnaires did not always read the brochure.

Potential Industrial Uses

METALLURGICAL INDUSTRY

The market for radioisotope instruments in metallurgy is limited, but the applications are very important industrially. In this field, light elements, e.g., silicon and aluminum, are often associated with those of medium weight, e.g., iron and calcium. All the large firms use emission spectrometers, whose performance is such that their users have become very exacting. However, the spectrometers are rather costly, and some laboratories are considering cheaper and simpler instruments for determinations where less precision is required. The smaller metallurgical firms do not generally use physical methods of analysis, and some do not use any analytical methods at all. Analytical equipment would be useful, but their budgets do not permit expensive apparatus.

In alloy analysis, three to six elements are determined, either simultaneously or successively at 5- to 10-min intervals, with 1 to 5% precision. Some of the elements that have a large physicochemical effect are present in very low concentration, and there are often interferences, especially in ferrous alloys. Continuous measurements are not common, and determinations are usually made in the plant. Grading of stored piles of alloys is of some interest. Apparatus for this would not need to show exceptional performance. It should, however, be selective because, especially in ferrous metallurgy, interferences are possible.

The potential market in electroplating firms is large, but these are usually small firms whose budgets do not allow expensive control apparatus. The maximum number of elements determined in any one bath is two, but bath compositions vary widely. Apparatus must therefore be able to determine a large number of elements, in different baths, in order to be rapidly amortized. The complex baths now used often contain organic compounds, e.g., wetting agents and reagents to give luster to the surface. For precious-metal baths, which are not complex, simple apparatus can be used.

For control of coating thickness, the possible applications in a given firm are sufficiently similar that in most cases only one measuring apparatus is needed. The coatings and their bases vary in thickness from 1 to 1000 μ, and continuous measurements are common.

CHEMICAL INDUSTRY

In basic chemicals manufacture, numerous applications are possible, but apparatus for determining several elements would be required if the market is to be extensive. Although frequently only a single element is determined and rarely more than two or three in one sample, numerous elements, of widely varying concentrations, are determined in different samples. The matrix may be gas, liquid, or solid, and precisions between 1 and 10% and lag times no longer than 5 to 15 min are required. Continuous process control is of interest in some cases.

In the chemical-conversion industries—petroleum, artificial textiles, rubber, and soap making—the possibilities for plant apparatus seem good, and continuous analysis is of some interest. Only one or a few elements must be determined, but the method should be able to determine all elements concerned in a process. The solid or liquid matrixes generally contain light elements. Concentrations vary over a wide range and may be very low. However, the problem of determining elements in low concentration seems capable of solution and in some cases has already been solved, e.g., cobalt in hydrocarbons.

In the chemical industries making products for consumption—food, pharmaceuticals, and dyes—the problems are large, but few justify radioisotope-based analytical methods because of the low concentrations of the elements to be determined. The single problem that appears of interest to the radioisotope equipment manufacturer is the continuous determination of a hydrogenation catalyst in the manufacture of vegetable food fats.

In the glass, refractory, and cement industries, only a few elements have to be determined, the most important being Al, Si, Ca, and Na. Several elements

may be determined either simultaneously or successively in less than 15-min intervals. Concentrations, as well as required precisions, are in the 1 to 10% range. One cement producer has solved the problem of continuous calcium determination. The problems are few, but they are serious and are posed by the very large firms who have no major financing problems.

MINING INDUSTRY

Rarely does more than one element, with a concentration of about 1%, have to be determined in the mining industry. The determinations concern standard minerals, where atomic numbers are greater than 20, and may be for continuous control during ore processing. Continuous measurement of the ash content of coal is an important problem, and a solution to this problem would ensure markets in both the extractive and user branches. Portable apparatus for prospecting or extraction would be of great interest because of the obvious disadvantages of having to take samples and send them to the laboratory from the field. Selectivity does not have to be so good as in metallurgy because there is rarely any interference. The conditions of use require, in every case, sturdy equipment and independent operation.

Factors Found Important in the Survey

The survey indicated certain essential points that must be taken into account in planning research or development work on instruments containing radioisotopes. Some of these directly affect the determination, some are gross characteristics of the instruments, and some are inherent in the marketing situation.

FACTORS DIRECTLY AFFECTING THE DETERMINATION

Sensitivity. A lower concentration limit of 0.1% seems generally satisfactory. The matrixes and the elements are very diverse, and not enough work has been done in most cases to fix the measurement limits. Systematic tests should be made to find the limits for the largest number of elements in the largest number of matrixes possible. Then it would be necessary to try to attain a 0.1% limit for as many situations as possible.

Selectivity. Although in many cases the selectivity of a proportional or scintillation counter is sufficient, this is not the case in the economically important field of ferrous alloys. Most of the elements added to these alloys have an atomic number between 22 and 30, and interferences are numerous. A solution to this problem does not seem to be immediately forthcoming, although an assembly of suitable sources and radiation filters should be satisfactory.

Precision. The precision required by industry is usually between 1 and 10%, but a reexamination of the processes would undoubtedly show that these requirements are not always justified. In most cases a statistical counting precision can be attained which is compatible with the precision of the measurement and the speed with which results are needed. Where ambient conditions are very severe, the stability of the electronics and the proportional counters may have to be improved.

Calibration. When binary mixtures are to be analyzed, the apparatus should be calibrated and checked periodically. When different elements are determined in different matrixes, the signal should be compared to that of the standard. When the mixture contains three elements but there is little variation in the matrix and no interfacing elements are present, the problem is the same as that of a binary mixture. If the matrix does vary and the elements in it affect the analysis, graphs must be made or a computer used. If the matrix effect modifies the results significantly, the application of the method to an analytical problem may give misleading results. Therefore matrix effects must be studied for each proposed application. Without such preliminary studies the method could be completely discredited.

Multiple Determinations. The inquiry showed that equipment that can be used to determine several elements is necessary if the method is to become widespread. Apparatus that could make successive determinations in a short time would, in general, be satisfactory.

INSTRUMENT GROSS CHARACTERISTICS

Dependability. One of the most important characteristics of analysis and control equipment is sturdy construction, particularly in field models. Transistorized electronic assemblies exist which enhance dependability, but they must be protected from humidity, corrosion, and vibration. A simple thermoregulator system should be provided. Scintillation rather than proportional counters should be used when possible. Some industrial users complained of the poor mechanical and thermal behavior of these detectors, but, because of the intrinsic qualities that make them good laboratory counters, they should also be useful in industry and therefore should be developed further.

Ease of Manipulation. Apparatus for plant use should be designed for operation by a person with little training. The accessibility of regulators to the operator should be reduced to the indispensable minimum. If different elements in a certain atomic-number range must be determined with the same measuring head, apparatus should be readily and easily adjustable. The results should be read simply,

for example, on a recorder or a galvanometer graduated directly in percentage.

Sample Preparation. Sample preparation should be eliminated unless absolutely necessary. If pulverizing or tabletting of samples proves necessary, apparatus should be developed which can eventually be automated.

Safety. The use of control apparatus containing radioactive sources poses safety problems. In general, the source activity and radiation energy are low enough that the operator is protected by a thin layer of shielding. Source storage does not pose any serious problems. However, direct exposure to a source could not be tolerated, and the measuring heads would have to be equipped with a system that prevents the source from being uncovered before the sample is in place. The user must not be able to demount the source, and radioactive elements that present serious contamination dangers in case of destruction of the head should not be used.

Use of this equipment in the large firms does not pose particular problems since, in the great majority of cases, these firms already use radioactive gages. However, it should be remembered, at least at first, that lack of information, the need for controlled protection against radioactivity, and the necessity of an administrative procedure will limit the use of this equipment in smaller firms.

MARKETS

In the survey an attempt was made to find suitable prices for the different types of equipment as a function of their performance and the new possibilities that they offer. About 30,000 francs ($6000) for laboratory or plant apparatus would be about a quarter of that of standard radioisotope-based apparatus or of the least costly emission spectrometer. If it saved one technician, it could be amortized in 2 to 3 years, including operating costs. Firms that do not already have analytical services probably could not afford this equipment either. For the maximum market the price should not exceed the cost of equipment for a small chemical laboratory [estimated as 15,000 francs ($3000)] even though its operating cost would be less than that of a chemical laboratory. This lower limit is theoretical and probably could not be reached.

A price of around 10,000 francs ($2000) for portable apparatus was estimated. Such apparatus could be considered expendable if no more than this was invested in it and could perhaps replace the existing analyzers in small firms. The price that could be spent for continuous industrial control apparatus depends on the importance of the process to be controlled and the value of the product.

It is normal to ensure service after apparatus has been sold, but, for sources whose half-lives are not very long (^{55}Fe, ^{109}Cd, or ^{153}Gd), a replacement service similar to that for ^{192}Ir sources used in gamma radiography should be provided. Service should also be provided for studying the users' problems, orienting the client, and defining the operating techniques that would have to be used. (Martha Gerrard)

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Summary of Symposium on Radioisotope Tracers in Industry and Geophysics in Prague, CSSR, Nov. 21–25, 1966

By F. J. Miller

Abstract: Speakers at the symposium on Radioisotope Tracers in Industry and Geophysics in Prague reviewed many uses of radioisotope tracers in industrial studies and the various aspects of geophysics. Specific, individual cases in which radioisotope tracers were proven valuable were also presented by authors from 18 different countries. The topics for the sessions of the symposium were industrial applications of radioisotope tracers, friction and wear studies, geophysical applications, dispersion of effluents (miscellaneous applications), and plant kinetics.

The many and varied uses of radioisotopes in industry and geophysics were presented at the symposium on Radioisotope Tracers in Industry and Geophysics in Prague, CSSR, Nov. 21–25, 1966. The 47 papers by 112 authors were contributed from 18 countries, with England and France being the most prolific. All of the papers are listed in the reference section of this review. As can be seen from the paper

titles, the use of radioisotope tracers in industry and geophysics is no longer a novelty. Tracers are now completely accepted as working tools, and they are used where no other method applies, where they offer a more expedient and elegant solution to a problem, or where their use is more economical than other methods. The versatility, expediency, and economy of radioactive tracer methods are shown by the wide variety of uses described.

The conference was divided into sessions that covered industrial application of radioisotope tracers, friction and wear studies, geophysical applications, dispersion of effluents (miscellaneous applications), and plant kinetics.

Industrial Application of Radioisotope Tracers

In the first paper of the first session, Postnikov,[1] of Moscow, surveyed the use of radioactive tracers in industry. Because the very widespread use of tracers made it impossible to cover the complete field, he covered only selected areas. Among the topics studied were the investigation of wearing surfaces in engine components, the abrasive effect of dust on engines, diffusion and self-diffusion, purity of materials, automatic control of processes, beer production, leak testing, and transport of material in pipelines.

Beswick,[2] one of the scientific secretaries of the symposium and presently serving with the Industrial Applications Section of the Division of Research and Laboratories of the International Atomic Energy Agency (IAEA), surveyed the routine industrial uses of radioisotope tracers in many countries of the world. As can be seen in Table 1 of the Appendix, many of the uses are common to all countries, but a few applications have been adapted to the unique requirements of certain countries. Table 2 of the Appendix shows the various isotopes suggested for use with gases, solids, and organic substances, and the chemical form in which they are used.

Friction, Corrosion, and Wear

Fodor,[3] of the Institute for the Development of Vehicles in Budapest, Hungary, used radioisotope tracers to investigate phenomenons that could affect engine wear. Although a decrease in wear could be effected by improving the quality of lubricating oil, fuel, and construction materials, the most significant factors affecting engine wear were the quantity of dust in the air and the efficiency of air filtration.

Chleck,[4] of Parametrics, Inc., Waltham, Mass., discussed the use of kryptonated materials in wear and corrosion studies of interest to industry. Kryptonates are defined as solids of all types into which the radioactive noble gas, ^{85}Kr, has been stably incorporated. Kryptonates may be prepared either by bombardment with ions of the gas or by simple heating of the object under an overpressure of krypton.

The experimentally verified fact that a Kryptonate heated to a given temperature loses a certain fraction of its activity and, after cooling, heating to any temperature below that temperature causes no further loss of activity can provide a means of temperature measurement. The method is uniquely useful for determining the temperatures to which moving engine parts have been subjected. There is no interference with operation of the engine. The operating temperatures of turbine blades in jet engines have been successfully measured in this way.

A further property of Kryptonates is the loss of activity from the surface of a kryptonated solid because of a disturbance in the lattice structure. In the course of a chemical reaction occurring on such a kryptonated surface, the lattice is destroyed, distorted, or transformed; any of these changes results in a loss of krypton activity. The extent of oxidation of a metal surface, or oxide-film formation (a type of corrosion by oxygen), may therefore be estimated by monitoring the decrease in radioactivity of the kryptonated surface. Reactions with any other corrosive gas or liquid can be followed with equal facility.

In addition to providing a relatively simple technique for following a corrosion rate, the measurement of Kryptonate activity affords a means of determining the rate constants of reactions that take place on the surface of a kryptonated solid.

The study of the complicated processes of friction and wear can be greatly facilitated by the use of kryptonated solids. Not only fundamental aspects of the phenomenons but also problems of immediate technological interest can be explored with this technique.

Radwan, Rewenska-Kostiuk, and Wezranowski,[5] of Warsaw, devised an activation analysis method for investigating wear by the inclusion of activatable elements in the wearing parts. The wear particles are subsequently irradiated in a reactor, and the amount of these present is determined by the induced activity. "Mischmetal"—a mixture of the rare-earth elements Ce, La, Nd, Pr, Sm, and Y—was used as the tracer in an amount so small that no structural change was caused in the material studied. This technique is useful not only for studying the wear of iron and steel objects but also for polyamide bearings, to which previously known methods of wear study are not applicable.

Methods of determining certain nonmetallic inclusions in ball-bearing steels were also worked out by use of activation analysis. Rare-earth oxides were used to simulate nonmetals. The study was aimed at ascertaining the effect of vacuum extraction and induction stirring on the extent of inclusions in the steel melt. The indicating rare-earth elements were

separated from the dissolved steel test specimens by an oxalate precipitation with calcium added as a carrier. The iron present was held in solution as the soluble oxalate complex. Abraded material in amounts of 1 μg can be determined.

Gervé,[6] of the Technische Hochschule at Karlsruhe, Germany, devised a method for simultaneously measuring three activities in engine oil that resulted from the wear of three different parts. Coincidence counting of gamma quanta registered on a NaI(Tl) crystal was the method chosen, with special arrangement of equipment to reduce Compton scattering and to separate the overlapping photopeaks of isotopes emitting similar gamma-radiation quanta. The continuous method of measurement is designed to investigate simultaneously the wear of any three of the following: (1) the chromium surface of a piston ring, (2) the iron sides of the same ring, (3) a second cobalt-alloyed piston ring, (4) an iridium-alloyed cylinder liner, and (5) a specially marked place. This counting method could also be used in neutron activation analysis to facilitate analysis of special chemical processes and to observe complicated processes of metabolism.

Burianová and Heijmánek,[7] at the Motor Car Research Institute of Prague, CSSR, stated that one of the most important problems in their work is the study of durability of parts. Most attention has been given to the heavily loaded crank-case-gear and piston mechanisms. They installed reactor-irradiated engine parts in a wear-test engine and measured the gamma radiation from the radioisotopes ^{59}Fe, ^{54}Mn, and ^{124}Sb in abraded particles suspended in the engine oil. The oil can either be pumped continuously through a counting chamber, or thief samples may be taken at intervals and counted. The study has shown that piston ring and bushing wear is caused by frequent change in the manner of operating the engine and that the wear curve is interrupted and shifted by oil changes. Laboratory test measurements and field measurements could be compared only generally.

Donhoffer and Duftschmid[8] studied wheel-flange wear of railway vehicles with ^{198}Au (obtained by irradiation of $HAuCl_4$) colloidally suspended in lubricating oil. An increase in axle loading and the higher speeds of modern trains have increased the wear of wheel flanges tremendously. Without proper lubrication the wheel tires would have to be replaced every 30,000 km. The lubricating oil must be dispensed in small quantities and only to the flange; excess quantities or application to the rolling surface would decrease the friction necessary for driving and braking action. As a result of the studies, a pendulum pump was devised that would feed oil only during lateral motion of the train such as would be experienced in traversing curves or at high speeds on straight tracks. Two scintillation probes fitted to the pivot mountings of the first and third cars scanned only the flange of one wheel of these cars. A portable scintillation probe measured the activity on all wheel flanges when the train was stopped at terminals. Autoradiographs were made to show the distribution of the gold on the wheel tires. A small G-M tube monitored the activity of the oil in the cylinder pump so that an accurate record of pump operation was obtained.

Geophysical Applications

Mott and Dempsey,[9] of the U. S. Atomic Energy Commission, reported a comprehensive survey of radiotracer applications in geophysics in the United States. The review evaluated the present position of radiotracer techniques with emphasis on the extent of use, practical limitations, and competition from alternative methods.

Alekseev and Srebrodolsky,[10] of the Ministry of Geology in Moscow, discussed a few of the chief uses of radioisotopes in industrial geophysics, such as:

1. Investigation of producing wells to determine the annular circulation and technical conditions in casings
2. Investigation of injection wells to determine water formations and check on conditions in casings
3. Determination of the height of the cement top in cementing of casings in deep wells, especially in areas of elevated temperature

They concluded that the use of radioisotopes makes possible the maintenance of the continuity of well operation and can actively influence the progress of work in individual oil and gas deposits as well as in entire oil fields. Tritium was found to be most useful for tracking the dynamics of underground water movement and studying the hydrodynamic relationship between individual formations in a productive series. The savings resulting from the use of isotopes was estimated at tens of millions of rubles ($\$1.10 \times 10^7$) annually.

Lévêque and Vigneaux[11] used autoradiography in France to study the changes in rocks under stress. Test rocks were injected with solutions of ^{59}Fe, ^{35}S, or ^{32}P. The autoradiographs taken after the rocks were subjected to test cycles showed, by the presence of microfissures, the changes that occurred in the rocks. These changes are important in predicting the stability of foundations of large civil-engineering projects, building construction, and rock piling.

One technique used to keep oil wells productive is to maintain an underground pressure by gas injection. Gondouin, Comier, and Thiberge,[12] in Algiers, studied the efficiency of the procedure by mixing radioactive tracer gases—tritiated methane, ethane, propane, and butane—with the injection gas. Because of the large volumes of gas and oil involved, relatively large amounts of activity (200 curies) and very sensitive methods of detection were required.

When the gas is injected simultaneously into several wells, the gas–oil displacement can be checked if the origin of the gas reaching the producer well from one of the injection wells could be established with certainty. Tracer injection and detection established the time between injection into the pressurizing well and arrival at the production well. With this information, uniform displacement of the oil by injected gas could be maintained.

Jirkowski,[13] at Ostrave, CSSR, used the radon, occurring naturally in soil gases, to establish whether or not there were any potentially dangerous faults, fissures, or other geological flaws in prospective dam-site areas. He found geological disturbances in the Sance-Recice, which cut across the Ostracive River, but the foundations of the dam in the Dalni Becna were intact. He concluded that the radioactivity test method was an economically sound and precise one for locating structural flaws in the earth's surface.

Comanescu et al.,[14] in Bucharest, Romania, studied the labeling of petroleum products in pipelines as a means of separating petroleum products of different qualities and as a method of measuring pumping rates. The isotopes ^{131}I, ^{65}Zn, ^{2}H as D_2O, and stable Cd were used. Cadmium naphthenate, which is easily prepared and is soluble in the petroleum products, was injected into pipelines and activated at the measuring point by a Po–Be neutron source and then detected by gamma counting. The radioactive tracers were detected by gamma spectrometry, and the D_2O, by interferometry. The D_2O method avoids handling of radioactivity and does not contaminate the pipelines.

Transport time of water or gas from an injection well to a producing well was measured with ^{131}I, ^{65}Zn, and D_2O.

Dispersion of Effluent

Harremoes,[15] of the Danish Isotope Centre at Copenhagen, is concerned with the increasingly important problem of pollution of waterways by waste discharge. Radioactive tracers were used in studying the capability of the receiving water body to dilute and disintegrate the deposited wastes. Work has been carried on since 1959 on labeling of water masses with tracers for study of dispersion and dilution. He hopes to develop an adequate theoretical model so as to minimize the expense of detailed field work. A contract has been set up with IAEA to review and correlate all published material for comparison with theoretical work.

Experimental work was carried out with the use of radioactive tracer ^{82}Br (as NH_4Br) distributed on the surface or injected at various depths. The dispersion and dilution pattern of the isotope was followed by a boat equipped with counting devices and navigational equipment suitable for establishing the exact locations of the vessel. The location and design of municipal sewer outfalls will be based on the data obtained from the radioactive tracings of the adjacent water bodies.

Guizerix et al.,[16] in a joint study by the Nuclear Center at Grenoble, France, and the Oceanographic Center at Nice, discussed the shortcomings of present mathematical models proposed to describe the turbulent dispersion of the soluble phase of effluents discharged into rivers. They used radioactive tracers—chosen after a comparative study of fluorescent rhodamine dyes and radioactive tracers—to test the models.

Nakasa and Ohno,[17] in Tokyo, chose neutron activation analysis to investigate air pollution by sulfur dioxide from industrial areas, and they worked on the assumption that a tracer substance would behave the same as stack gas. The assumption is probably valid if the size of the tracer particles is very small. A water solution of cobalt sulfate was sprayed into the base of a plant stack. The mean diameter of cobalt sulfate particles emerging from the top of the stack was measured to be 3 μ. At seven sampling points, located at distances up to 10 km from the stack, large volumes of air were filtered through "millipore SC" filter papers. The dust samples thus collected, together with the filter papers, were irradiated with a thermal-neutron flux of 1.7×10^{12} n/(cm^2)(sec) for 15 hr, cooled for 3 weeks, and measured for radioactivity of ^{60}Co by scintillation spectrometry. The cobalt was determined at the level of 5×10^{-8} g with an accuracy of 10%. The advantages of the cobalt sulfate tracer method are the absence of radioactivity and toxicity hazard, the convenience of an analytical method without chemical processing, the economy, and the adaptability to high-background regions, such as industrial areas. Correlation was good between ground-level concentrations of sulfur dioxide measured chemically and those derived from stack gas tracing by cobalt sulfate and Freon-12 gas.

The concern of the wood-pulp and paper-mill industry with stream pollution and its reduction led Chatters and Peterson,[18] of Washington State University, to consider the use of radioisotope tracers to evaluate processes and effluent control. Lanthanum, an element not usually present in wood and readily estimated by neutron activation analysis, was incorporated in the wood pulp. The use of this nonradioactive but readily activated element eliminated the problems of handling of radioisotopes in a mill and of preventing their reaching public waterways. The lanthanum-impregnated wood pulps were quantitatively detectable at all collection points in the plant, even where initial ratios were 3 lb of treated to 40,000 lb of untreated fibers.

Pulp that had been irradiated could also be used as a tracer by following the induced activity of ^{56}Mn, ^{38}Cl, ^{24}Na, and ^{64}Cu. Detection is still possible in a dilution of 1:10,000 for 16 hr after irradiation. This technique is peculiarly suitable to the study of

effluents from the digestion and bleaching of wood pulp. In addition to the wood fibers themselves, the material removed from the pulp could be studied.

Miscellaneous Applications

Houtman and Medema,[19] at the Reactor Institute at Delft, Netherlands, extended Richter and Gillespie's[19a] work on the use of ^{14}C-labeled carbide as a reagent for the detection of water in gases. Richter and Gillespie had shown that the reaction of $Ca^{14}C_2$ with H_2O to produce labeled acetylene and subsequent counting of the acetylene could be used to detect water in a flowing gas stream. Houtman and Medema studied the parameters of the system and, by systematically adjusting them, were able to achieve reproducible results. The data presented in their paper clearly demonstrated the usability of the radio-release method based on the reaction with ^{14}C-labeled carbides for determining water-vapor concentrations in gas in the range of 1 μ to 20 mm Hg. The radiation hazard involved in the technique can be minimized by suitable choice of the specific activity of the carbide bed. Conditions can be set such that the maximum permissible concentration in a room of 200 m^3 volume is not exceeded if the air is changed only once in 8 hr.

Churchill,[20] with Atomic Energy of Canada Ltd., Ottawa, presented enough cases to prove the usefulness of $^{124}Sb-Be$ neutron sources, particularly in the production of short-lived isotopes. Such a device for industrial uses is of particular importance to Canada—a country in which distances are vast and reactors are few and inconveniently located. The neutron flux of 10^9 n/(cm^2)(sec) of a $^{124}Sb-Be$ source enables the carrying out of activation analysis and the production of isotopes for tracking processes. Specific applications studied were ion exchange with ^{60}Co, separation of europium from gadolinium by electrolysis into a lithium amalgam, and activation analysis of steels, ores, and coal samples.

Anguenot,[21] of the Centre d'Étude Nucléaire de Saclay, France, reported the continuous measurement of oil consumption in an internal-combustion engine. Tritiated squalene, a high-boiling hydrocarbon, was added to the lubricating oil. A bypass line from the engine exhaust sampled the gas through an ionization chamber kept at 150 °C to prevent condensation of the water vapor. (Higher specific activities were necessitated by use of an ionization chamber than would be needed with scintillation counting, but this disadvantage was largely offset by the advantage of continuity of measurement.) The method has been in the laboratory development phase for 2 years but is now sufficiently well developed that plans are being made for use of the method on a vehicle in normal operation.

Ljunggren,[22] of the Isotoptekniska Laboriet of Stockholm, Sweden, reviewed the use of tracers for evaluating material-flow parameters in industrial plant and natural systems. Examples of the use of tracers given were:

1. Measurement of flow parameters under well-defined conditions of flow, velocity, and volume flow rates
2. General examination of the characteristics of flow patterns, paths, etc.
3. Measurement of dilution caused by dispersion of dissolved or suspended matter
4. Evaluation of process and equipment performance.

He discussed the principles of the various methods and also dealt with a theoretical evaluation of the use of tracers to investigate material turnover.

Rotkirch, Kommonen, and Castren,[23] in Helsinki, Finland, developed mathematical models of various process units and systems. They presented data-handling methods for the interpretation of results obtained from a tracer investigation, which permit improvement of the process by control of critical parameters.

Männistö and Niemi,[24a] of the University of Oulu, Finland, discussed the dynamics of a cellulose-bleaching plant. Tracer experiments were carried out in the bleaching operation of a cellulose sulfate plant to determine flow patterns for the cellulose fibers and to develop dynamic models in time and frequency domains[24a] for the various parts of the process. Batches of activated glass fibers were injected instantaneously to generate an activity pulse, and the resulting activities in the pulp were measured continuously as instantaneous impulses at several points along the line. The time integrals of the record, corrected for radioactive decay, were normalized to obtain residence-time distribution functions. Computer methods were developed for the calculations, with programs prepared in ALGOL computing language.

Ljunggren,[25] in his second paper of the meeting, developed a mathematical treatment for the study of flow conditions in industrial process vessels. Information obtained by the use of radioactive tracers was essential to formulating the relations which permitted calculation of the recirculating fraction of flow as well as of the mean and variance in the distribution of residence times corresponding to a rapidly injected sample of tracer at the inlet. The analysis was developed and used to evaluate a number of tracer tests on the circulation of cooking liquor through the chip bed in a continuous digester. As tracer, $^{24}NaHCO_3$ was used in amounts that varied between 2 and 10 mc for each run. The mathematical relations developed made possible the obtaining of consistent results from the experimental data.

Bullock, Johnson, and Whiston,[26] in Durham, England, used radiotracers in what they consider the most valuable application in the chemical industry—

the determination of flow characteristics for reaction and process vessels. Tracers enable the assessment of residence time and its distribution so that design values can be checked and process efficiency improved. Practical examples given include a study of an olefin hydroformylation reaction using ^{140}La naphthenate; xylene isomerization using ^{140}La acetate; gas–liquid reactions using *p*-dibromobenzene (^{82}Br); and an isopropanol process using ^{82}Br as either ammonium bromide or *p*-dibromobenzene.

Bujdosó,[27] from Budapest, Hungary, demonstrated the advantage of the radioactive tracer method not only in developing the right technology but also for planning continuous systems. The example quoted in his study was the preparation of alumina using ^{65}Zn to follow the process. Better stirring was achieved, and several vessels were eliminated from the continuous production line.

Kulcsár,[28] at the Heavy Chemical Institute at Veszprem, Hungary, studied the conditions of material flow by the isotope method in two research-type chemical reactors and in commercial equipment such as the mixers of a superphosphate plant and a calcium carbide plant. The first research study was carried out on a film reactor that contained rotating cylinders pressed against the walls of a cylindrical vessel. A liquid introduced at the top of the apparatus forms a film between the inner surface of the body and the outer surfaces of the rotating cylinders and flows to the bottom of the reaction vessel where it is removed. Phosphorus-32 in aqueous solution was injected. The results showed that the average residence time reached a plateau as the revolution rate of the cylinders increased and that film thicknesses were lowest at a medium rate of rotation—400 rpm.

The operation of a gas–liquid column contactor for the preparation of 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline (Niflex) was studied to determine the fate of the iodine catalyst. A liquid mixture of phenetidine and acetone containing the iodine catalyst is introduced at the top of the column and acetone vapor injected at the bottom. Residence times were obtained by injecting ^{32}P in acetone solution. The results were checked with ^{131}I and showed that essentially all the iodine remains in the liquid phase. In an apparatus used for superphosphate production, improved mixing was achieved as gaged by the residence time of injected ^{32}P. The introduction of a baffle plate and alternate counterrotation of the mixers considerably improved the quality of the superphosphate, with accompanying economic gain.

Phosphorus-32 was also used to study the factors involved in furnace operation to produce calcium carbide. Information obtained led to a decision to rebuild the furnace with a reduced effective volume. Increased productivity and improvement of product quality are anticipated.

Bondy, Robin, and Vidal,[29] from France, discussed the industrial use of activatable tracers in metallurgy, glassmaking, and ceramics. The method is of interest because of the diversity of problems that can be studied and the ease of application to industrial processes. All such experiments involve certain fundamental steps: (1) analysis of blank samples, (2) choice of tracer element, (3) choice of chemical or physical method of introducing the tracer, (4) product labeling, (5) sampling, (6) activation analysis, and (7) interpretation of the results. The diversity of applications is shown by the listed examples:

1. Labeling of lubrication oils for subsequent identification
2. Study of bubble transport in distillation columns
3. Study of distribution times for materials in a glassmaking furnace
4. Study of the distribution of textile oil on a textile thread
5. Measurement of the displacement time of products in an oil-refinery unit

Hoffman et al.,[30] in Warsaw, Poland, were concerned with the movement of a caprolactam polymerization mixture through continuous polymerization equipment. Uniformity of the end product required that all components of the polymerization mixture remain in the equipment for the same length of time. Movement of the mixture through the equipment was monitored by labeling a small amount of caprolactam with ^{82}Br or ^{24}Na and using a scintillation counter. The effect of various design features of the equipment was thus determined, and the kinetics of movement of the caprolactam polymerization mixture were ascertained.

Akerman and coworkers,[31] in Warsaw, Poland, chose volatile germanium-organic compounds labeled with ^{77}Ge to investigate processes in petroleum refining. The germanium-organic compounds were first synthesized and then activated in a neutron flux of 10^{13} n/(cm^2)(sec) for 1 to 5 hr to produce the required amount of activity. Counting was carried out 12 to 15 hr after activation. The recording apparatus was placed at suitable points outside the equipment walls, and the passage of the labeled gas was easily detected. Reflux circulation time was determined with tetraethyl germanium. Tetra-*n*-amyl germanium (^{77}Ge) was used to measure the linear rate of movement of petroleum in heating ovens. This work demonstrated conclusively the suitability of germanium-labeled compounds for following refinery processes. Further work is planned to exploit this capability.

Hirayama, Osada, and Hamada,[32] in Tokyo, Japan, also reported on the analysis of processes by use of radioactive tracers. A double-labeling procedure was devised to test the effectiveness of the labeled compound in following the process. Radioactive ^{32}P and inactive gold were introduced into the feed stream of a carbon-black plant, and the activity due

to ^{32}P was determined immediately after successive sampling at intervals of 5 min at five points. Aliquots of the same samples were irradiated in a nuclear reactor, and the gold content was assayed by counting the ^{198}Au. The residence times and flow patterns obtained with the different techniques gave the same results. Useful information was thereby obtained concerning the time required in switching the process from one type of oil to another.

The determination of diffusion properties of gases moving at high speeds can be an awkward problem. Krypton-85 was used to check the diffusion properties of nitrile gas in the precipitation tower of the nitrile process. The ^{85}Kr was injected at the top of the tower, and its discharge at the tower outlet was marked by continuously photographing a NaI(Tl) scintillation detector. Adequate information was obtained even though the residence time was only a few seconds.

Akerman and his coworkers,[33] in Warsaw, also used radioisotopes to study the electrolytic reduction of aluminum and magnesium. The economics of the process were considerably improved by process changes made after consideration of the results of the isotopic studies.

Kato, Sato, and Inoue,[34] at the Institute of Industrial Science of the University of Tokyo, Japan, investigated the flow and mixing behavior of electrolytes in an electrolytic nickel refinery by means of a radioactive tracer technique. Sodium-24 or ^{82}Br were used as Na_2CO_3 or NH_4Br, respectively, which did not interfere in any of the chemical reactions taking place. Residence times of the electrolyte in various parts of the refinery process were measured.

Eriksson, Erwall, and Nyquist,[35] in Stockholm, Sweden, have carried out a research project initiated by the Swedish Ironmasters' Association to assess the possible applications of radiotracers. The four different fields studied were:

1. Determination of slag weight
2. Determination of the origin of nonmetallic inclusions
3. Labeling for identification
4. Material transport in the blast furnace

Slag weight was determined by using the isotope dilution technique with ^{131}Ba or ^{140}La.

The same isotopes were used to determine nonmetallic inclusions in steels, with lanthanum preferred since the possibility of its reduction and transfer into the steel is less than with barium.

The labeling of slags, mortars, and ceramic materials was given considerable study. Slags were labeled with rare-earth oxides. Mortar was labeled by simple addition of a water solution of $^{140}La(NO_3)_3$ and drying. Ceramic materials were labeled by neutron irradiation of the actual objects by impregnating with $Tb(NO_3)_3$, reburning, and then irradiating with neutrons long enough to achieve a sufficiently high level of radioactivity. Steels were labeled with either ^{182}Ta or ^{192}Ir, or both. Other isotopes such as ^{99}Mo, ^{122}Sb, and ^{198}Au have been used to mark different quality steels.

Transport of material in a blast furnace to determine the position of coating buildups on furnace walls was studied by introducing ^{140}La as a tracer. The active material, incorporated in a capsule of stainless steel encased in a graphite cylinder, was introduced at the top of the furnace. The decrease in intensity from the top down was shown by gamma-ray scanning.

Kubin et al.,[36] in Prague, CSSR, described a method for measuring the retention time of materials in production lines. A radioactive tracer was instantaneously injected at the input end of a flow line, and the distribution of activity at the output measured as a function of time. The form of the curve depends on the parameters of the installation and its mode of operation.

Liquid-phase investigations were carried out on laboratory models of chemical vessels with scintillation detectors and a screened probe. A water-soluble salt of ^{131}I was used in the study of the industrial extraction of aqueous phenol by butyl acetate. The retention time for the aqueous phase in various sections of the column was easily ascertained without interrupting the flow.

Houtman, Kuiper, and Beek,[37] in Delft, Netherlands, developed data on the residence time of materials in laminar flows and of granular solids passing through rotary kilns by use of radioactive tracers. Laminar flow is especially important in the extrusion and molding of polymers and in the coating of wires with plastics. Polymer fractions flowing faster than others may have different properties because the polymerization process or degradation reactions go on during the process. Corrections applied to the results obtained from the pulse injection of a gold sol into the polymer result in fair agreement between the measured distribution curve and the calculated residence-time distribution.

The movement of sand through a rotary kiln was checked by the injection of sand impregnated with radioactive $AuCl_3$. Houtman et al. concluded that the motion of the granular material could be regarded as plug flow, i.e., all grains of sand having the same mean velocity.

Balla and Csetenyi,[38] in Budapest, Hungary, used ^{51}Cr to observe flow patterns in a continuous glass melt, and the paths taken by it were detected by sampling at various points in the furnace. The tank furnace is 6 m wide and 40 m long with burners and regenerators on both sides. The main parts are melting area, refining area with two floater blocks, and two channels. Each channel supplies three automated drawing machines. From the data, Balla judged that the flow rate was highest at the center of the tank. Fifty-six percent of the melt flowing along the

side of the tank is from material fed in on the same side, and the remaining part is from the other side. Twenty-four meters from the feed pocket in which the tracer is injected the flow is uniform across the whole cross section of the furnace. The flow rate in the two channels depends on the ratio between the glass production of the left- and right-side machines.

The choice of ^{51}Cr as a tracer isotope was predicated on the basis of its 27.7-day half-life, easily detectable gamma radiations, low dose rate, and relatively high value of "maximum permissible concentration" in industrial material (MPC = 2×10^3 $\mu c/cm^3$). In addition, the chromium oxide is soluble in the glass melt and is nonvolatile.

Clayton, Spackman, and Ball,[39] at Wantage, Berkshire, England, considered the accuracy of liquid-flow measurement using radioisotopes. Accuracy is limited by the nature of the hydraulic system and by instrumental errors in the measuring equipment. Means of minimizing errors by shortening mixing distance were discussed. The best techniques allowed a consistent attainment of accuracy to within 0.2%.

Dahl and Thomassen,[40] at Kjeller, Norway, applied a radioactive tracer technique to the measurement of water flow through a turbine to assess the efficiency. A sealed plastic vial containing ^{131}I was placed in a side-opening steel container. An electrical detonating cap, placed between the vial and the closed side of the container, was set off remotely and completely disintegrated the vial, instantaneously dispensing the tracer. The water was sampled at intervals or in a single sample contained in a 50-liter drum and the activity measured. Water flows below 20 m^3/sec could be readily measured by the single-sample method, and greater flow rates, by the multisample, discontinuous method.

Berry, Clayton, and Webb,[41] of Ottawa, Canada, and Wantage, Berkshire, England, overcame the difficulties of measuring flow characteristics in a high-speed gas-reaction vessel by using ^{85}Kr. Six millicuries of ^{85}Kr were injected into the vessel by a high-speed injection system, and the outgoing gas was routed through a sample line, passing through a plastic-phosphor detector. An ultraviolet stripchart recorder continuously registered the radiation intensity. The accuracy of the mean residence time was determined to within 5%.

Johnson,[42] in Durham, England, applied the dilution principle to the measurement of gas flow rates in large-scale chemical processes. Xenon-133, together with a carrier gas, was bled into the plant gas stream at a known, constant rate. Samples taken from the gas stream were fed through a cold trap, and the ^{133}Xe was recovered by flushing with inactive xenon and counted. Flow rates of about 10^6 m^3/hr were measured to 1% with a ^{133}Xe activity of 100 mc.

The tracer technique is useful for locating small leaks in plant apparatus where entry of undesired liquids or water vapor into the gas stream occurs.

Guizerix and Baeza,[43] of France and Argentina, did a theoretical analysis of data obtained from the injection of tracer at the input of a continuous mixer and the variation in activity with time, at the outlet. The efficiency of the mixer can be related to the analyzed and corrected curves.

Williams and Howell,[44] at Port Talbot, Glamorgan, England, were concerned with the mixing of the molten iron held in a reservoir prior to steelmaking. Contaminants such as sulfur, phosphorus, silicon, and certain other elements must be kept within reasonable limits for efficient control in the steelmaking process. The large reservoirs (known as "mixers"), in which the molten iron is kept, should reduce variations in the impurity content of the individual ladles provided that good mixing takes place. If radioactive iron of known specific activity is added to the iron in these reservoirs, the specific activity expected to be present in a sample of thoroughly mixed iron from the reservoir can be deduced. The deviation from the deduced specific activity indicates any departure from ideal stirring. Blast-furnace iron added to the hot-metal reservoirs was shown to mix satisfactorily.

Whiston,[45] at Durham, England, found that simple radiochemical techniques were of considerable assistance in solving problems arising in the development of chemical processes. The equipment used was uncomplicated and relatively inexpensive. Conventional methods would have required much more experimental effort and in some cases would have been totally inadequate. Examples of the use of ^{36}Cl, ^{35}S, and ^{14}C were discussed in detail for the determination of the fate of chlorine added to an oxidation system, the partitioning of sulpholane (tetrahydrothiophene 1,1-dioxide), and the determination of the relative rate of formic acid oxidation.

Mihics and Varga,[46] in Hungary, used the radioactive tracer ^{59}Fe to investigate the corrosion resistance of electrodeposited coatings. The deposition of iron impurity in electrodeposited layers of nickel on iron objects was determined with the local distribution of the iron being shown by autoradiography. The use of brightening additives diminished the amount of iron deposited. When $NaBF_4$ was dissolved in the bath, the amount of iron deposited was less than that laid down with brighteners only, but still considerable. Mihics and Varga, as a result of corrosion testing, concluded that corrosion was directly attributable to the iron content of the nickel plating. If objects made of iron are electroplated with nickel, iron is continuously dissolved into the bath and redeposited together with the nickel. The authors state that without the use of radioisotopes the investigations could not have been made.

Blanc and associates,[47] in France, selected a mixture of ^{186}Re and ^{188}Re as a suitable tracer for measuring the density of a water–steam emulsion in waterwall tubes of industrial boilers. Other isotopes

were rejected because their gamma-ray energy was too high, they reacted with water, or they were too long lived for industrial use. The information gained from gamma-ray scanning of the tubes was useful in diagnosing any impairment in the proper functioning of the tubes and in locating potential trouble spots due to corrosion. The measurements in no way interfered with normal operation of the boiler.

Appendix

Table 1 GEOGRAPHICAL DISTRIBUTION OF ISOTOPE USE

Countries	No. of organizations	No. of people employed	Isotope uses	Isotopes used
Austria	3	24	Leak detection	^{24}Na, ^{82}Br
			Air movement	^{85}Kr
			Flow rate	^{24}Na
			Mixing efficiency	^{24}Na
			Water movement	^{3}H, ^{131}I
			Oil exploration	
			Activatable tracers	
Canada	10	-	Oil-well investigation	^{131}I, ^{60}Co, ^{137}Cs, ^{192}Ir, ^{182}Ta, ^{46}Sc
			Leak detection	-
			Mineral dressing	-
			Solvent extraction	-
Czechoslovakia	250	150	Material transport	
			Flow rate	
			Leak detection	
			Chemical kinetics	
			Leak testing of transistors	
			Tire wear	
			Engine wear	
			Residence time	
			Oil-well cementation	
Hungary	4	-	Solidification and circulation	
			Furnace-lining wear	
			Contamination source	
			Purity control	
			Flow rate	
			Material transport	
			Flow pattern	
			Mixing	
			Leak detection	
Italy	68	-	Engine wear	
			Chemical processing	
			Metallurgy	
			Geophysics	
			Mixing	
			Residence time	
			Measuring of oil consumption	
			Hydrological–research	
Japan	Numerous	-	Engine wear	
			Refractory wear	^{60}Co
			Aluminum volume	^{198}Au
			Leak testing	^{85}Kr
			Residual pig iron	^{60}Co
			Hg in NaOH	^{203}Hg
Netherlands	15	57	Leak detection	
			Retention time	
			Mixing studies	
			Water migration	
			Silt and sand movement	
			Flow rate	
			Flow pattern	
Norway	2	10	Flow rate	
			Flow pattern	
			Dilution analysis	
			Pollution studies	
Philippines	2	6	Leakage location	
			Underground water	
			Catalyst flow	
Poland	7	120	Mining	
			Metallurgy	
			Chemical technology	
			Petroleum	
			Geophysics	
			Cementation of wells	
			Rock porosity	
			Material transport	

Table 1 (Continued)

Countries	No. of organizations	No. of people employed	Isotope uses	Isotopes used
			Process kinetics Leak location Wear tests Steel inclusions Charge movements	
Spain	3	20	Leaks and flow rates Hg content in NaOH Engine wear	^{131}I, ^{82}Br ^{203}Hg
Sweden	1	9	Furnace-lining wear Leak detection Paper machine testing Material transport Mixing studies Volume determination Effluent discharge River flow velocity Dispersion in receivers Wear in furnaces Labeling for identification Nonmetallic inclusions Slag weight	
United Kingdom	142	-	Material transport Mixing studies Volume determination Leak detection Effluent discharge Friction wear labeling	

Table 2 RADIOACTIVE TRACERS FOR VARIOUS MATERIALS

Isotope	Chemical or physical form
Radioactive Tracers for Gaseous Material	
^{41}Ar	Gas
^{76}As	AsH_3
^{82}Br	CH_3Br
^{85}Kr	Gas
^{133}Xe	Gas
^{35}S	H_2S
Radioactive Tracers for Solid Material	
^{24}Na	Na_2Co_3; polypropylene balls
^{46}Sc	Sc_2O_3
^{65}Zn	ZnO
^{51}Cr	Absorbed on quartz
^{64}Cu	CuO
^{198}Au	$AuCl_3$ adsorbed on powder
^{182}Ta	Ta_2O_3
^{144}Ce	Ce_2O_3
^{82}Br	$CaBr_2$ in polyethylene containers
Radioactive Tracers for Solid Material (Cont.)	
^{140}La	La_2O_3; polypropylene balls
^{110m}Ag	Adsorbed on solid grains
Radioactive Tracers for Organic Materials	
^{24}Na	Naphthenate; salicylate
^{82}Br	Bromobenzene; paradibromobenzene
^{140}La	Naphthenate
^{65}Ni	Stearate; oxalate
^{77}Ge	Various organic compounds
^{60}Co	Naphthenate
^{198}Au	Sodium cyanide solution; amine salt or colloidal form
^{131}I	I_2-kerosene; iodobenzene
^{124}Sb	Triphenylstibine
^{59}Fe	Ferrocene; dicyclopentadianyl-iron
^{35}S, ^{14}C, ^{3}H	Various organic compounds

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The following papers are all from the symposium, *Radioisotope Tracers in Industry and Geophysics*, that was held in Prague, CSSR, in November 1966 (IAEA publication STI/PUB/142). The symposium was sponsored by the International Atomic Energy Agency, and the IAEA designation of the paper is given. References 19*a* and 24*a* are taken from the papers cited in Refs. 19 and 24.

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AEC–DID Eighth Annual Contractors Meeting: Isotopes Systems Development

On Dec. 5–7, 1966, the AEC's Division of Isotopes Development (DID) held its eighth annual contractors meeting dealing with *Isotope Systems Development.** In the 3-day session, chaired by Dr. George J. Rotariu of DID, 39 reports of character work were presented, and there were four panel discussions. Eight presentations dealt with *Basic Technology Development,* with the remainder of the program covering *Systems Engineering: Analytical Methods; Marine Device Development; Environmental Applications; Industrial Applications; Aerospace Applications;* and *National Security Applications.*

The *Systems Development Program* was initiated in 1958 with the objective of accelerating the development of new principles and techniques of isotope applications, with particular emphasis upon public benefit problems. The objective has remained essentially the same over the years, but recently the Advisory Committee on Isotopes and Radiation Development has recommended that some of the effort be directed toward the assurance that the developed technology will actually be picked up and used.

Although major emphasis has been upon the *Systems Engineering* or direct applications area—particularly on those projects in which an end user is assured and on problems which solve significant problems in government and industry for which an end user is involved—DID continues to support unsolicited ideas in the areas of *Basic Technology* and *Analytical Methods,* despite the fact that end users may not be explicitly identified.

Basic Technology Development

Shipp of Oak Ridge National Laboratory (ORNL) reported work on the improvement of technology for making lithium-drifted germanium detectors for use in high-resolution gamma-ray spectroscopy. Aiming at a more consistent product, larger sensitive volumes without loss of resolution, and virtual elimination of "dead layers" that seriously limit detector efficiency for low-energy gamma rays, ORNL has developed a new ("U-drift") technique that reduces the drift time to about one-fourth that required by the more conventional planar technique. The resulting detector has contacts that are smaller and farther apart; thus the capacitances of detectors with large sensitive volumes can be made less than with planar-drifted detectors. Since the resolution of gamma-ray spectrometers normally increases as detector capacitance is decreased, this new technique is an improvement for making high-resolution detectors with large sensitive volumes. It was pointed out that two problems still plague workers in this field: the lack of a source of large germanium crystals with satisfactory properties and the controlling of the surface conditions of the detector. Minute variations in either have major effects on the voltage breakdown and leakage current of detectors. To date, typical ORNL detectors have been made with a sensitive volume of 6 cm^3 and a resolution of 3.5 kev (full width at half maximum) for 1.33-Mev gamma rays.

Trice of General Electric Company's Space Sciences Laboratory discussed the use of the surface-contouring effect to investigate avalanche or internal amplification in semiconductor detectors. Application of geometrical-surface field control overcomes semiconductor surface effects which, in the past, have been a barrier to achieving high fields over useful distances in $p-n$ junction counters. Contouring redistributes the charge so that the space-charge region is not "pinched." A $p-n$ junction "proportional" counter has been developed which displays sizeable internal gain and a room temperature signal-to-noise ratio similar to that of a photomultiplier tube. It is thus possible to detect and do reasonable energy analysis of soft X rays (measured to 0.06 kev) at room temperature with the detector coupled to a standard charge-sensitive amplifier displaying a higher noise level. The detector has the significant advantage of extreme speed of the avalanche gain and permits detection of 1.49-kev X-ray events concurrent with the flow of detector-leakage currents of over 100 μa. The scheme also is capable of extreme miniaturization and simplicity and operates over a wide dynamic counting range. A prototype detector is only 1 cu in. in volume and is capable of counting rates at low levels (e.g., soft X rays without the necessity for anticoincidence schemes) as well as rates in the vicinity of 10 counts/sec.

Mayer of Hughes Research Laboratories described attempts to obtain high-atomic-number semiconductor materials capable of use as particle detectors at room temperature for gamma-ray spectroscopy. Cadmium telluride is being studied because, in addition to showing good promise as a semiconductor, ingots can be grown containing large single-crystal portions. "Clean-room" facilities are being used to improve resistivity.

*Note: Since the meeting, DID has been reorganized owing to programmatic changes within the Commission. A chart showing the realignment of responsibilities can be found in *Isotopes and Radiation Technology*, 4(2): 199 (Winter 1966–1967).

Fergusson covered the work of Johnston Laboratories on basic development and applications of bubble chambers for low-level counting. By use of bubble chambers to improve sensitivity of detection of low levels of radioactivity, an order-of-magnitude improvement in detection of minimum specific activity could result, and many possibilities would be opened up in atmospheric and oceanographic research where samples are of low specific activity but unlimited in size. A simple manually operated chamber was designed to operate with a Freon filling. Data from this led to the design of an automatic chamber using liquid propane as the working fluid. The chamber is held at constant temperature and the surface temperature controlled by the degree of superheat pressure (bubbles smaller than a critical radius disappear; those greater than the critical radius grow).

Heath of Idaho Nuclear Corporation's National Reactor Testing Station reported on his expanded Gamma-Ray Spectrum Catalog, made necessary by the recent improvements in gamma-ray spectrometry afforded by the use of lithium-ion-drifted silicon and germanium detectors. He also reported on the improvement in resolution (e.g., 750 ev for 100-kev gamma rays) brought about by the use of field-effect transistor (FET) preamplifiers. The revised NaI catalog is expected to be available by fall of 1967, and the first volume of the germanium catalog by early 1968.

Toothacker of Edsel B. Ford Institute for Medical Research covered work on the use of ^{147}Pm to excite Kα radiation from iron, copper, and molybdenum and use of these radiations in aqueous-solution absorptiometry. The molybdenum 17.5-kev radiation works best of the three and is suitable with a 1-cm cell for detecting concentrations of various salts [e.g., $Ba(NO_3)_2$, $Pb(NO_3)_2$, and NaCl] in water. It can also be used in a 2-cm cell for estimating concentrations of alcohol–water mixtures.

Preuss, also of Edsel Ford, discussed X-ray diffractions with beta-excited sources (^{147}Pm with Cu, Fe, and Mo) as well as with the manganese Kα X rays resulting from the decay of ^{55}Fe by electron capture. Three diffracted beams from LiF (θ = 20 to 55°) were clearly demonstrated with the ^{55}Fe, but not with the ^{147}Pm sources on NaCl and LiF, at least up to 100 mc. Preuss also reported on the status of his compilation of "Beta-Excited X-Ray Spectra." This is covered elsewhere. [Isotopes and Radiation Technology 4(3): 243-249(1967).]

Sellers, reporting on a Parametrics (now Panametrics) contract, described his project designed to explore the basic technology involved in the generation of fluorescence X rays by alpha-particle bombardment and the areas of application of this technology. He used ^{210}Po for most of the work. Since the X-ray yield increases with decreasing Z, the technique is particularly useful for low-Z elements (e.g., below magnesium), although for higher-Z elements there is also some advantage owing to the absence of matrix effects. Analytical applications investigated included engine-oil contaminants (iron), fluorine-containing oils, and multielement analysis of a simulated moon surface (sodium to copper). Resolutions: C, 100%, N, 80%; O, 75%; F (Teflon), 57%; Mg, 43%; and Al, 35%.

Systems Engineering

ANALYTICAL METHODS

Lyon of ORNL briefly discussed several developmental programs of an analytical nature: (1) the use of a beta-excited light source, combined with pulse-height measuring equipment, to make high-precision photometric measurements; (2) the use of inorganic liquid scintillation phosphors—designed to increase the size of aqueous samples that can be assayed; (3) the application of neutron activation analysis to the assay of CaF_2 in fluorspar (at the 97% level) for the U. S. Bureau of Customs; (4) the measurement of the rates of release of tritium from tritiated self-luminous paints (which showed that the fraction released is very small under normal conditions); and (5) the development of nuclear data for new radioisotope products, many of which are of interest to the medical profession: ^{171}Tm, ^{123}I, ^{197}Hg, ^{188}W, ^{188}Re, ^{194}Ir, and ^{130m}I.

Rhodes covered the Texas Nuclear Corporation research dealing with the spectral and yield measurements of bremsstrahlung and characteristic X rays from ^{3}H absorbed in 15 different target materials. External acceleration of the ^{3}H beta particles is also being considered, since order-of-magnitude increases in intensities of the excited X rays are possible. Coincident with the work on generation of X rays is a study of the energy-resolution problem at low energies; it is apparent that practical X-ray filters are needed for elements silicon to scandium, inclusive. A prototype portable battery-operated X-ray analyzer is being built, using a NaI(Tl) scintillation counter as detector, which should be capable of field assay of a wide range of base-metal ores (e.g., Cu, Zn, Rb, Sn, Mo, W, Cr, Ni, Mn, and Ti).

Two reports on activation analysis covered (1) the Texas A&M work (in collaboration with the U. S. Department of Agriculture as a part of the general program of Public Benefit Demonstrations) on trace quantities of pesticide residues in soil and agricultural products (arsenic, mercury, and bromine in foliage, soil, fruits, hay, vegetables, etc.), reported by Kuykendall; and (2) the U. S. Geological Survey work, discussed by Senftle, involving in situ mineral exploration in which mobile 150- and 200-kev accelerators are used to generate neutrons in the field; the devices have been particularly successful for silver detection.

MARINE DEVICE DEVELOPMENT

Case of ORNL discussed the cooperative program involving DID, the National Aeronautics and Space

Administration, the Strategic Air Command, the U. S. Army Corps of Engineers, and others, in which the mechanics of littoral transport around Point Concepcion, Calif., are being investigated. Short-half-life isotopes such as ^{133}Xe and $^{140}Ba-La$ are being used to tag sand, and a detector device has been designed which is capable of rolling along the sand surface and over the rock projections that are common along the coastal area. This 3-year program is expected to develop sophisticated isotope techniques for studying sediment transport in general and for determining specifically whether littoral sediments are transported around a major headland at which the shoreline orientation changes ~ 90°.

The Lane–Wells contract, directed toward a determination of the technical feasibility of measuring both density and moisture content of unconsolidated sediments by means of a probe employing nuclear sensing devices, was reviewed by Youmans. A multipurpose probe is envisioned, which will operate on a multiconductor cable of the type used in well logging. Density is sensed by a gamma–gamma system, and moisture, by a neutron–neutron system, with a sufficient number of additional tests (e.g., natural gamma radiation, acoustic velocity, electrical conductivity, fast neutron activation) also being made to overcome the ambiguity introduced by the fact that it is almost impossible to differentiate between the hydrogen in water and the hydrogen in constituent clay minerals. Hopefully the device will not only establish the relative proportions of water and solids but will also identify the minerals in the matrix.

The Naval Oceanographic Office, in work described by Anderson, is involved in the development (for routine analyses of oceanic radioactivity) of a low-background beta detector system with rather stringent requirements: high counting efficiency for solid samples (present 600 to 900 min per sample is too long); provision for mounting foils for absorption measurements; provision for multiple detection within a single shield of minimum volume, but without cross detection; and an improved system for mounting samples for counting and for changing samples. Basically the system being constructed comprises four gas-flow beta counters connected in gas-flow series with 13 brass-walled Geiger tubes acting as an anticoincidence shield. The counters are 1.25-in. cylindrical volumes with single center wires strung across their diameters and double-faced gold-plated Mylar windows on the lower ends.

Somewhat related to this work is the program of the U. S. Naval Ordnance Laboratory, reported by Riel, in which an attempt is being made to show the connection between radioactivity and ocean conditions. This requires a measurement of oceanographic parameters, and, to this end, an attempt is being made to add sensors to an underwater radiation detector so that temperature and pressure can be measured simultaneously with the radioactivity. The present device measures depths to 270 ft, within ±2 ft up to 100 ft, and to within ±2% from 100 to 270 ft. Temperatures can be determined within ±0.5°F between 35 and 75°F.

Of interest to geochronology is the work of Queens College and Lamont Geological Observatory, reported by Thurber, dealing with the study of the distribution, in waters and surficial deposits, of the nuclides characteristic of the uranium and thorium decay series. The distribution measurements take advantage of the unique relationships provided by the decay series and make the nuclides useful as tracers for the study of oceanographic, hydrologic, and geologic problems. Among these are the use of ^{230}Th to determine the accumulation rates of deposits that form on the ocean bottom (e.g., manganese nodules and deep-sea sediments); the use of ^{230}Th, ^{232}Th, and uranium concentrations, by virtue of characteristic disequilibriums in phenocryst-bearing recent volcanic rocks, to find the time of eruption and possibly some details of the events prior to the eruption of a volcano; and a study of the origin of unsupported ^{228}Ra in seawater, both to find a mechanism for its generation and to study its possible use as a tracer of water bodies.

The U. S. Bureau of Mines (USBM) is vitally interested in getting a marine mining industry started and is supporting a Sea-Floors Minerals Program. Paydon reported on the USBM study to determine the feasibility of using nuclear and radioisotope techniques for delineation and characterization of marine mineral deposits and the control of mining operations. So far the work has centered about the in situ activation analysis of sea-floor phosphorite, manganese nodules, red clay, and sand (potentially gold-bearing). The long-range goal of the program is to develop a Mineral Detection Probe that will determine, from sea floor to bedrock, the vertical dimension of an unconsolidated mineral deposit (100 to 150 ft of sediment) and provide at least qualitative — and hopefully quantitative — analyses. This program is being continued under USBM sponsorship.

ENVIRONMENTAL APPLICATIONS

Smith, of the U. S. Department of Agriculture's Forest Service, explained work on (1) developing optimum nuclear systems for hydrologic research and (2) applying such systems in the study of ways to increase total water yield through manipulation of vegetation. A successful, permanently placed, gamma-transmission, profiling snow gage has been built, using a small gamma source and a crystal detector, a pulse-height-analyzer rate meter, an amplifier, and a chart recorder. Work is continuing on a system for measuring the water used by large plants such as trees. However, 50% of the 71×10^6 acre-ft of water from the area under consideration comes from snowpacks, and proper cutting of forests can delay snow melting for as much as 4 weeks.

Moisture lost through normal evaporation as well as through transpiration is also being investigated, by virtue of a companion contract with Hazleton–Nuclear Science Corporation, as reported by Essington, since many millions of acre-feet are known to be lost by these processes. Carbon-14-labeled hexadecanols in amounts of ~12 lb/acre are being tried. for example. on the snow surfaces. Rates of water movement in soils, under actual conditions, are being studied in order to tie down moisture regimes, and rates and directions of water movement.

Hansen, of the U. S. Bureau of Reclamation (WBR), reported on a joint DID–WBR 4-year program for using radioisotopes to measure flow of water through high-head turbines and other hydraulic machines. The overall program includes (1) a study of the fluid mechanics of tracer mixing, radioisotope injection, and the sampling of the isotope–water mixture; (2) a study of the selection and handling of the radioactive tracers; (3) development of a measurement system using the techniques established for radioisotope handling, the fluid-mechanics parameters, and the methods of data interpretation; (4) field tests of the techniques for making accurate discharge measurements. Gold-198 has been used so far, and ^{82}Br will also be used in future tests; approximately 1 curie per test is usually involved. Radiorelease techniques are also being considered for stream-flow measurements.

Hansen also reported on a radioisotope study of reservoir leakage at Anchor Reservoir in Wyoming. High water losses through one very large sinkhole and other outlets originally limited reservoir capacity to about 10% of maximum; remedial measures reduced losses to a minimal level. However, other leaks have developed, and WBR is investigating the use of radioisotope techniques (1) to solve the Anchor Reservoir leakage problem and (2) to develop new or improved methods of field investigation which can be used early in the study of proposed reservoir sites in order to prevent the problems experienced at Anchor. Approximately 60 curies of ^{3}H were introduced into the reservoir (equivalent to ~ 4000 TU*), and measurements are being taken in four drill holes (>1000 ft deep) around the reservoir to determine the direction and velocity of flow in each of the holes at the period of maximum reservoir storage and again after the reservoir has drained and the groundwater has reached a steady state.

The DWICA (Deep Water Isotopic Current Analyzer), which has been reported on at previous contractors' meetings, is now being evaluated by TVA at Fontana Reservoir, N. C., as reported by Elder of TVA. The Model 1B device is being used in studies of the internal hydrodynamics of the thermally stratified reservoir; it can measure and record velocities down to 0.003 ft/sec at depths to 400 ft. It is particularly advantageous under conditions of unsteady flow, since there is no response lag due to inertial effects. Some disadvantages encountered are the large size and weight, the difficulty in positioning it motionless relative to the ground, its requirement for electric power, and the long time required to obtain a velocity profile.

Chatters, of Washington State University, outlined a program designed to evaluate the potential application of radioisotope techniques to stream-pollution problems in the pulp and paper industry. The objectives are twofold: to obtain a better understanding of the source of stream pollution originating in the pulp and paper industry, and to aid in the reduction of pollution through in-plant process control. Salts of various kinds (Cu, Ag, Zn, Ba, and La) have been tried, with lanthanum being the most satisfactory. The procedure consists in adding lanthanum nitrate to pulp, in conjunction with normal rosin-size suspension, giving tagged fibers suitable for tracing. Subsequent dilution of the tagged fiber—3 lb to 40 thousand lb of untreated pulp—gives material that can be employed effectively in following the fibers through the mill. Samples taken at appropriate points were neutron activated and analyzed.

Ziegler of Panametrics, Inc., described a self-referenced X-ray absorption radioisotope gage for continuously monitoring sediment concentrations (1000 to 50,000 ppm) in rivers and streams. A 1.3-mc source of ^{109}Cd is used, with a proportional counter for a detector. Twelve units are currently being tested by members of the Inter-Agency Sedimentation Project, and results indicate excellent prospects.

The problem of monitoring buildup of methane concentration in mines is being studied by Melpar, Inc.; the work was reported by Finkel. A cross-section ionization detection system has been developed comprising two detectors—each containing 2 curies of tritium ($^{3}H/Ti$)—in the basic detection system. Each detector, consisting of two parallel TiT_2-coated foils (one of which is connected to a direct-current power source and the other to a direct-current-coupled amplifier), will produce an output signal whenever the gas composition, pressure, or temperature changes. Only the concentrations of methane and water vapor will vary significantly in the usual coal mine, and, since the detector is insensitive to water, the temperature or pressure variations can be "nulled out" to give a device specifically responsive to methane. A concentration level of 1% activates an indicator light; at 2% a second light and an external control circuit are actuated. The latter may be used to provide an auditory warning or to shut off power to the mining machinery. The lower limit of detection is ~0.2% methane.

The problem of converting to a usable level the high-voltage direct-current power available in most U. S. mines apparently can be overcome by use of high-voltage power transistors.

*1 TU = 1 atom of ^{3}H per 10^{18} atoms of ^{1}H.

INDUSTRIAL APPLICATIONS

The Texas Nuclear Corporation (TNC) on-line nuclear-analysis study was reported by Martin. The application of neutron analysis techniques, including activation analysis and inelastic scattering with fast neutrons, to the on-line measurements of elemental concentrations in various materials (both bulk and liquid) has been under investigation using the nuclear-analysis pilot-plant facility jointly sponsored by TNC and DID. Experimental studies have involved on-line analysis (dynamic testing) of both coal and bauxite and static testing (i.e., on nonmoving samples) of a number of materials. Early experiments with coal revealed low signal-to-background ratios in the prompt (carbon and oxygen) channels, resulting in lower-than-expected sensitivities. Since modified shielding alone did not improve the ratio sufficiently, an anti-coincidence detector was inserted in order to reduce the neutron-induced as well as Compton background in the prompt spectrometer. A series of measurements of the aluminum and silicon content of bauxite at varying belt speeds revealed that (1) a very good statistical yield of gamma rays from both silicon and aluminum could be obtained with a neutron flux slightly in excess of 10^8 n/(cm^2)(sec); (2) corrections to the aluminum and silicon counting yields were necessary due to the interference of the gamma rays from iron (about 11% by weight of the oxide); (3) at the higher belt speeds, the ^{16}N activity from the oxygen caused interferences (as expected); and (4) there was a slow buildup of total delayed gamma-ray activity (due to feedback in the closed-loop configuration). The silicon and aluminum contents were measured with accuracies of 3% and 6%, respectively. Most of the error was due to the poor statistics in the iron yield used in the correction of the silicon and aluminum content. Without the presence of iron, the counting statistics were sufficient to permit the detection of a change of only 0.03% silicon and 0.3% aluminum. Generator life at 10^9 n/sec is ~100 hr.

Wood of Kaman Nuclear discussed a new contract directed toward the development of an industrial installation and operating techniques for activation analysis on liquid systems. Kaman will demonstrate applications of activation analysis to materials in pipelines, perfect the techniques required for in-plant installations, and finally install one or more systems in industrial plants to demonstrate interest in, and acceptance of, activation analysis as an industrial technique. Some of the analyses and materials considered are nitrogen in protein (food products); bromine and chlorine (pesticide residues) in food products; nitrogen, phosphorus, and potassium in fertilizer; fluorine in water; sodium and phosphorus in detergents; fluorine and oxygen in organics; oxygen in polyethylene; initial impurities and wear products in oil; vanadium in oil; and metal ores in slurries. It is believed that a recirculating closed loop can be used to increase sensitivity of low-level activity by buildup. Expectations are that oxygen can be determined in concentrations of 1 to 5 ppm, nitrogen at about 1%, vanadium at ~0.1 ppm, and other metals at ~ 1 ppm.

The Bureau of Mines, as reported by Armstrong of the Bartlesville Petroleum Research Center, is involved in the development of a prototype design for a low-level radioactive gas-tracer system for use in the natural-gas industry. A feasibility study has been completed to determine the environmental conditions and performance requirements for an instrumental system of this nature, and filling-gas tolerance limits were determined for a proportional counter using methane as the predominant filling gas. A prototype unshielded low-level proportional-counter tube assembly was constructed and evaluated; on the basis of the data obtained, specifications and design suggestions were assembled and a request for proposals was written. The continuance of the work is awaiting construction and delivery of the instrument. No problems have been encountered which, in their opinion, should prove to be insurmountable in the design of a practical system. To date, all effort has been directed toward the development of the detection portion of the system because it is felt that no real problem exists in the injection of a radioactive tracer into a natural-gas system, provided that facilities for determining the injection level periodically are available at the site.

The availability of high-intensity ^{55}Fe sources has raised the possibility of using isotopic sources rather than X-ray machines for portable diffraction measurements. This study, reported by Semmler of Illinois Institute of Technology Research Institute, has examined the feasibility of using ^{55}Fe for field measurements of stress using diffraction techniques. An extremely simple geometry was arranged to use pulse detection, and, although the ^{55}Fe source had an output only about 3% of that assumed on the basis of the delivery information, diffraction lines were immediately observed in both the forward and backward directions from iron samples using only 1-min counting periods at each angular setting. Counting rates were of the order of 150 counts/min, and the angular difference between diffraction lines was easily determined to within 0.2°. Even with poor resolution, the diffraction lines from worked and stress-relieved samples showed some evidence of line-broadening effects. The geometry used was far from optimum and is capable of considerable improvement. In the course of this program, various parameters have been experimentally measured, e.g., photon output of the source, angular distribution of the radiation, sensitivity of Polaroid film to manganese Kα radiation, attenuation of manganese Kα radiation by components in a Polaroid camera, comparative response of intensifier screens and various phosphors, and X-ray-

machine beam intensity. A study of diffraction geometries and collimation systems has also been made to determine the feasibility of using sources with a large area rather than the typical line or point source from an X-ray machine. In terms of the original application to stress analysis, the outlook is not too promising because of the low intensity and, more importantly, because of the poor location of the diffraction lines. In general, however, the outlook for radioisotopes in highly portable diffraction equipment with modest resolution is very good.

Weller of Franklin and Marshall College discussed work on the development of methods for industrial-control measurements of low-level radioactive contamination of materials. The bulk of the effort has been devoted to finding commercially available equipment directly suitable for, or readily adaptable to, low-level radioactive contamination-control methods that have adequate sensitivity and are simple and economical enough for use in an average industrial laboratory. The primary goal is to find the instrumentation best suited to the problem. However, since many laboratories have some alpha- and/or beta-measuring apparatus on hand, it was highly desirable to ascertain the practicality of the use of such instruments for low-level contamination control. Therefore comparative studies on instruments commonly available in radioisotope laboratories were included in the investigation. The results show that there is sufficiently sensitive and yet economical apparatus commercially available to perform the type of radioactive contamination monitoring required.

AEROSPACE APPLICATIONS

The zero-gravity radiotracer propellant gage work of the Nuclear Technology Department of TRW Systems was described by Rusch. A small quantity of ^{85}Kr gas is injected into the ullage space of the propellant-filled tank. As propellant is expelled from the tank, the ullage-space pressure is maintained by a regulated influx of nonradioactive pressurant gas. This gas influx dilutes the concentration of the radiotracer gas, which is continuously measured with radiation detectors. The pressurant gas within the tank's ullage volume forces propellant expulsion. The count rate from the detectors, being proportional to the ^{85}Kr concentration, is related to the volume of propellant remaining by means of a simple algebraic equation. The count-rate data can be converted into a digital quantity readout or used as input for propellant management. The gaging error was consistently less than 0.5% over the entire range of propellant volume. Analytical studies of full-scale system hardware showed the radiotracer system to be potentially superior in weight, accuracy, and simplicity to other zero-gravity gaging systems under development. Low-permeability bladders are required to prevent gaging errors due to loss of krypton from the propellant-tank ullage space. Further, the use of Parylene C (with a low attenuation) is recommended to protect detectors from a corrosive propellant environment; it has allowed semiconductor detectors to operate up to 600 hr in an N_2O_4-vapor environment.

Goodman of Panametrics, Inc., covered the development of an interstage hydrogen-detection system for the Saturn vehicle, involving a radiorelease technique in which hydrogen is detected by measuring the release of gaseous ^{85}Kr which occurs during the hydrogen reduction of a kryptonated metal oxide (such as PtO_2) containing a few millicuries of ^{85}Kr. A program of design, development, and construction of a hydrogen-detection instrument based on this technique and compatible with the Saturn rocket has been undertaken. Based on the results of an investigation of all the factors involved (e.g., response time, sensitivity, accuracy, pressure and temperature dependency, vibration and noise effects, and safety aspects), a system design will be selected, and a breadboard system conforming to this design package will be constructed, tested, and evaluated. A final modified system embodying any approved design revision will then be constructed. Preliminary results with a kryptonated platinum dioxide sensor have shown excellent sensitivity to hydrogen in the range of 0.1 to 3.0% by volume and to response times of the order of 0.5 sec. This is suitable, since 1% hydrogen is the lower limit of explosibility. One possible drawback is the lifetime of the Kryptonate, since it is "used up"—the higher the hydrogen concentration, the shorter the lifetime.

Two reports were presented on a project dealing with nucleonic fuel gaging for aircraft. Snowball of the Air Force Flight Dynamics Laboratory, Wright-Patterson Air Force Base, discussed the overall picture. The objective of the program is a demonstration (through in-flight test) of practical feasibility of continuous measurement of fuel-mass quantity in aerodynamic fuels with minimum errors resulting from attitude and tank-geometry variation. The nucleonic approach, being basically mass sensitive, should reduce or eliminate the errors resulting from (1) variations in flight attitude from the principal calibration attitude and (2) normal changes in tank geometry. For a shallow fuel tank, it should reduce these errors by broad-area coverage of the tank with sources and solid-state detectors. Further, it is possible that attitude- and deformation-induced errors can be further minimized by in-flight compensation using available flight data. The nucleonic approach is expected to be about five times as accurate as the presently used systems over large attitude excursions. This approach should also provide a more reliable system. The three phases of the program include: (1) An engineering investigation of the basic problems of application of the nucleonic approach, including a computer analysis to develop analytical techniques to determine the number and placement of

detectors and sources. Consideration will be given to cross-talk, buildup, effects of plumbing and tank structure, and application to various types of tank construction. Silicon, gallium arsenide, and cadmium telluride detectors will be examined. Gamma sources will be selected on the basis of suitability for typical applications, size, weight, half-life effects, stability, initial cost, source strength, and safety. Primary consideration will be given to radiological health hazards. (2) The formulation of the design of a flight-test system, fabrication of flight-test systems, establishment of a flight-test plan, and environmental laboratory tests of flight hardware. (3) Flight tests on a large cargo aircraft that has representative problems in gaging with respect to attitude errors and wing-deflection errors.

Gibson of General Nucleonics Corporation discussed the experimental part of the program:

Computer-Program Source-Detector Location—defining the problem for a generalized tank configuration and setting up a computer program to simulate the scale-model tank that will be used later in scale-model tests. The empirical results of the scale-model tests will then be compared with the computer-program results and the program revised as necessary. Empirical results of the modifications for attitude and wing-deflector compensation will be compared with the computer program and revised. Then the final program will be compiled for application to various tank shapes and dimensions.

Detector Design—evaluating diffuse silicon and $p-n$ junction silicon detectors, including new types of detectors that result from other work, for example, the cadmium telluride device of Hughes Research Laboratories. If necessary, the detectors will be tooled with peltier devices.

Source Design—evaluating ^{60}Co, ^{137}Cs, and ^{85}Kr either as point sources or as line sources.

Scale-Model Test Program—preparing a large-sized test bed and davit system suitable for various tank sizes, capable of providing attitude changes of 20° in both pitch and roll, and designed so that the tanks can be distorted.

System Analysis and Design—using information from the preceding steps of work: basic-system air analysis and air apportionment, preliminary source-detector mapping study, attitude air analysis, attitude-compensation mapping studies, establishment of tank deformation as a function of flight parameters, revision of air analysis and air apportionment to reflect attitude and deformation compensation, design study of deformation compensation, and design of a volumetric measurement approach.

NATIONAL SECURITY APPLICATIONS

Two forensic papers covered the use of activation analysis in "Scientific Crime Investigation" and "Criminalistics," respectively. Guinn of General Atomic Division of General Dynamics Corporation discussed a number of new exploratory studies of (1) bomb-detonation residues, (2) documents and faded photographs, (3) photonuclear activation analysis of various evidence-type materials, (4) activation-autoradiography of certain types of evidence materials, and (5) radiotracers in various forensic problems. In-depth studies are well under way on the subjects of the trace-element characterization of specimens of paint and paper, with large numbers of samples from various known sources being examined in detail by purely instrumental (nondestructive) high-flux thermal-neutron activation analysis (NAA). This will give a catalog of results and a large body of analytical data that will permit a meaningful statistical analysis to serve as the basis for making sensible and accurate statements when actual evidence samples of paint and paper are compared by this technique. A similar in-depth study of specimens of glass is also in progress, but the results are less promising, and the relatively small amount of additional comparative information obtainable—compared with that obtainable by regular forensic comparative methods for glass—may not warrant an extensive study. A similar statistically large number of results are being obtained on hand-blank values and gunshot-residue values to provide a body of data from which firm statistical conclusions can be drawn in actual cases in which gunshot residues (barium and antimony) have been determined by the NAA procedure. Studies with rifles and shotguns, measurements with tagged gunpowder, and radiotracer studies are also being continued.

Pro of the Laboratory Branch, Alcohol and Tobacco Tax Division of the Internal Revenue Service (IRS), covered work on applications of NAA to the study of physical evidence, with efforts divided between the examination of specimens from actual casework and research problems connected with various types of materials frequently encountered as physical evidence. The Post Office Department and Bureau of Narcotics are actively using reactors for the irradiation of specimens connected with forensic work and are utilizing the gamma scintillation-counting systems located at the IRS laboratory in the subsequent analysis of the radioactive materials. This combined effort resulted in the examination of more than 580 cases involving about four thousand specimens, and it is anticipated that these agencies will continue to cooperate in the same manner for several more years. This work has demonstrated that nondestructive NAA offers great potential for the examination of a large variety of physical-evidence specimens and is particularly useful for the characterization of very small specimens, especially those consisting largely of an organic matrix. More than 18 cases have been introduced into federal and state courts by the IRS, and it is significant to note that many other cases never went to trial because the defendant entered a plea of

guilty when confronted with the laboratory findings. In several other investigations, the laboratory examination of the physical evidence resulted in voluntary surrender of vehicles and other personal property used in illicit activities. Specific research during the year dealt with: (1) Bullet-residue transference to various materials, which showed that antimony and copper residue from the explosion of a pistol cartridge is deposited on the bullet surface and that NAA could be used to measure the residue wiped from the bullet surface onto various target materials in passage. (2) Comparison of adhesive tapes, which indicated that NAA can be employed to characterize tapes through their elemental compositions. Differences between manufacturers as well as batch-to-batch and in-batch variations were measured. (3) Soil comparisons, by means of which the IRS hopes to determine the probability that two soils come from the same location if the composition of both soils is the same. By determining the concentration ranges and distribution of the elements, a method of probability calculations will be developed and applied to soils from actual cases. A sample grid (13 samples symmetrically taken over a diameter of 600 ft) was chosen to determine the extent of trace-element variations between soils taken close to each other and to study group-to-group variations as a function of distance. (4) Paint comparisons, which will differentiate between paints of the same color produced by different manufacturers. In addition, this study will determine the extent of batch-to-batch and in-batch variations that may exist. (5) Trace-element composition of heroin, in which more than 300 heroin samples, known to have been produced in many illicit laboratories throughout the world, are being compared by NAA, with the objective of determining the extent to which the raw materials and process equipment used in the production of heroin add characterizing trace elements.

Sellers of Panametrics, Inc., reported on a project applied to the forensic work, in which X-ray-fluorescence techniques are being investigated for possible application to problems involving national security and law enforcement. Six applications currently being studied are grading of fluorspar, identification of Teflon, and identification of precious metals (Bureau of Customs); tagging of stamps and stamp-machine ink for automatic mail sorting (Post Office Department); identification of bullet holes (FBI); and covert (nonapparent) marking, e.g., map marking (for a number of agencies).

Discussions

In addition to the contractor presentations, there were two general discussions covering, respectively, "Trends in Semiconductor Technology and Applications" and "Trends and Requirements in Oceanography."

TRENDS IN SEMICONDUCTOR TECHNOLOGY AND APPLICATIONS

Panel, moderated by Hitch (AEC–DID), comprised Guinn, Heath, Mann (ANL), Mayer, Miller (Bell Telephone), Morgan, Polishuk (Air Force), Rhodes, Sellers, Senftle, Shipp, and Trice.

Polishuk suggested that, for Air Force application, high resolution is less important than good counting devices, which should be stable over a range of −40 to +100°C (and occasionally 300°C). Small size and weight and low power consumption are important. Avalanche devices at high temperature are also needed.

Morgan indicated that the specific application at hand was often the determinant factor. Large-volume (e.g., lithium-drifted germanium), low-capacitance, high-speed (~2 nsec) crystals are needed. He also suggested that a 1-kev background in X-ray spectroscopy, although tolerable in the 10-kev range, is rather serious in the 1- to 5-kev range.

Heath felt that gamma-ray spectroscopy (from 10 kev to 10 Mev) using field-effect transistors is in relatively good shape at present. He believes that improved lithium-drifted silicon detectors could do many jobs now reserved for lithium-drifted germanium, but *without cooling*. He also bemoaned the fact that detectors still are not up to the state of the art of electronics. A good detector (5 cm^2 by 5 mm) should be able to resolve <1.5 kev for ^{137}Cs (now, at best, probably only 5 kev).

Miller suggested a need for better (p^+,n^+) contacts and good carrier transport (1% measurement consistency over 1 mm thickness). He noted that germanium is easier to work with than silicon and that 10^{10} impurities of germanium per cubic centimeter can be made, which would allow shipment without cooling and cooling only during use.

Rhodes indicated a need in fluorescence X-ray work for crystals 10 cm^2 by several millimeters thick.

Mann pointed out that it is hard to justify 5-kev germanium at this time. The detector limit now is ~1.5 kev at 1 Mev (full width at half maximum). He also mentioned that some European crystals are better than those in this country.

Sellers put in a plea for X-ray detectors in the kiloelectron-volt region, which would be rugged and operate at room temperature. For example, the moon probe needs to operate down to the sodium 1-kev X ray.

Senftle said that for his work it was necessary to get rid of the liquid nitrogen.

Mayer felt that the recombination or trapping centers controlled lifetime, not structure per se.

TRENDS AND REQUIREMENTS IN OCEANOGRAPHY

Panel, chaired by Magin (AEC–DID), consisted of Thurber, Anderson, Case, Pedrick (Naval Oceanographic Office), Johnston, and Johns (Ocean Science &

Engineering Corp.). Pedrick suggested that it may be hard to justify the use of isotope systems as replacements for the older "tried-and-true" (and often satisfactory) methods. He pointed out that the apprehension of the public toward radioactivity and radiation is, in itself, a deterrent to isotope usage and suggested that the use of tracers in ocean streams may actually be only a long-range "wish."

Anderson, replying to a question concerning the need for in situ measurements, said that in situ measurements *are* necessary, since a "thief" cannot be depended upon to bring up a liquid that is *identical* with that sampled (i.e., pressure, temperature, organisms, etc.).

Thurber emphasized the need for better analytical methods, suggesting that whether these are isotopic or not is of no significance; however, he feels that the isotope methods seem to offer more hope than most others, particularly for trace-element analysis.

Johns observed that the funding policies for oceanography are not too satisfactory—probably primarily because the ultimate beneficiaries do not understand the significance. On the other hand, the nuclear scientists are not really conversant with the problems of oceanography. Some method is needed for mutual evaluation.

Johnston reiterated the need for better and more accurate methods of analysis (also indicating that they need not necessarily involve isotopes). He also suggested that more work needs to be done in taking advantage of "worldwide tracers" (^{14}C, fallout isotopes, etc.). Lastly, he referred to the need for giving specific consideration to what he termed "sea-lab" problems, specifically related to oceanography.

In a special session Thatcher, of the Water Resources Division of the U. S. Geological Survey, reported on the UN-sponsored *International Hydrological Decade*, indicating that part of the program required the accumulation of certain types of fundamental information as related to (1) neutron moisture techniques and loggings; (2) geochronology and hydrology measurements (^{2}H, ^{3}H, ^{18}O, and ^{14}C); (3) groundwater tracer techniques; and (4) stable isotopes (D, O, etc.).

Adler and Trombka of Goddard Space Flight Center discussed the role of nucleonics in aerospace. (It was suggested that the best way to get to the moon is to pile up all the feasibility studies.) Under the heading of *analytical techniques*, Adler emphasized the need for *total systems* to be used in orbiter exploration. Specific instruments are not enough—the problem of handling the information obtained is serious and must be resolved. He briefly outlined the problems of the geochemical explorations by man on the moon, indicating that, for one thing, although the availability of (e.g., alpha-emitting) isotope probes would be helpful in selecting surface samples, the astronaut still needs an intelligent *basis* for that selection. Second, since there probably will be only a limited time available, strong emphasis must be placed on speed.

With respect to the technology involved in these investigations, Trombka reported on the current availability of a portable multichannel analyzer, which shortly will be equipped with a memory. Also available are portable linear amplifiers, although not really high-grade yet. In the milliwatt range, they weigh ~200 g, without amplifier, and can be reduced to ~50 g.

He indicated that remote sensing and both charged- and uncharged-particle analyses would be necessary and postulated that inelastic-scattering, prompt-gamma, and die-away techniques would be applicable to later missions where traverses are involved.

(P. S. Baker)

Section

IV

Isotopes and Radiation Technology

Food Irradiation

Cost-Benefit Study of Selected Products in the Atomic Energy Commission's Low-Dose Food-Irradiation Program

Abstract: A detailed cost-benefit study by Daniel Yankelovich, Inc., has recommended that the USAEC give firm support to research on irradiation of New England finfish and Hawaiian papayas, marginal support to research on Hawaiian mangoes, and no further support to research on Dungeness crab, Alaskan king crab, and bananas. The analysis was based on 310 interviews with industry personnel and 627 interviews with consumers. Government research reports were studied, and an attempt was made to arrive at real numbers for projected costs and benefits. Benefits will be increased sales and reduced spoilage losses. The report is summarized and reviewed.

Articles have appeared in the popular literature[1-2] reporting the finding of Daniel Yankelovich, Inc., that housewives will accept irradiated food without question when it is approved by the Food and Drug Administration (FDA) and marketed under well-known brand names. This finding was one of the results of a study[3] undertaken by Daniel Yankelovich, Inc., for the U. S. Atomic Energy Commission (AEC), who asked the Madison Avenue firm to determine whether or not AEC should continue research on radiation processing of six foods and, if further research was advised, to recommend the level of research that could be justified.

As a result of their cost-benefit analysis, Daniel Yankelovich, Inc., recommended that research on irradiation of New England finfish and Hawaiian papayas be given firm support, that research on Hawaiian mangoes be given marginal support, and that research on Dungeness crab, Alaskan king crab, and bananas be stopped. The following article is a review and summary of the report.

The answers to two questions were sought: Can the public benefits associated with AEC's investment in research and development of radiation processing of foods equal or exceed the cost to the taxpayer? What is the likelihood that industry and consumers will act to promote commercialization of the process? A favorable answer to either question does not assure a favorable answer to the other one.

Scope of the Study

The AEC specified that New England finfish (cod, haddock, flounder, and sole), West Coast Dungeness crab, Alaskan king crab, bananas, Hawaiian papayas, and Hawaiian mangoes were the specific products to be studied. These products were selected because the state of their irradiation technology was relatively well advanced and because of their "representativeness." The Yankelovich study emphasizes that this report is a study of only six foods; the results of the study cannot be extrapolated to the whole food-irradiation program. Benefits from radiation processing of each product are unique to that product and its marketing problems. This study is, in fact, six case studies.

Radiation processing is most likely to find commercial application, given technological feasibility, when products meet the following criterions:

1. The product is a large-volume, perishable staple so that success is not contingent upon creating a market for the product.
2. The product is subject to spoilage losses sufficiently great to be a widespread, openly recognized problem.
3. The product is relatively high priced so that reduction of spoilage cost is sufficient incentive to support radiation processing costs.

Timing of FDA Approval

The single most important factor affecting commercialization of radiation processing of any of the six foods studied is approval from FDA. The AEC has assumed the following dates (updated in proof) for FDA approval of these foods:

New England finfish	Late 1967
West Coast crabs	Undetermined
Bananas	Undetermined
Papayas and mangoes	Mid-1971 to mid-1972

As the Yankelovich study explicitly states: "All of the study's projections and conclusions about timing stand or fall on these dates and, of course, the program as a whole stands on FDA approval sooner or later."

The FDA officials declined to comment on the timetable because (1) petitions have not been received for five of the products, (2) a basis for predicting whether or not petitions will require additional data does not exist, and (3) information from many different sources must be evaluated.

Study Methodology

The study was conducted in three parts: qualitative discovery phase, quantitative survey phase, and analytical phase. In the first phase, AEC contractors and management of leading firms dealing with the products were interviewed, and AEC contractor reports and other government-agency research reports were reviewed. The objective of this first phase was to identify the size of the problem, to determine how the technical benefits of radiation meet the food industry's needs, to find out what awareness of radiation existed in this industry, and to get some idea of consumer attitudes toward irradiation of food.

In the second phase the data-gathering effort was extended to a larger base. Almost 1000 interviews were conducted: 627 with consumers, 37 with management at national headquarters of the largest supermarket chains, 60 at local units of the largest supermarket chains, 86 at local units of other food stores, 87 with restaurant managers, and 40 at various institutions.

The third phase was an attempt to quantify the costs and benefits that could result between now and 1980 from commercialization of food irradiation. The conclusions were tested by calculating net benefits from a range of values for key variables.

Consumer Attitudes

The overall picture of consumer attitudes is one of acceptance, but with reservations. The level of awareness is low: 24% of the consumers claimed awareness, but only 6% correctly grasped the concept of radiation processing of food. Initial response of those claiming awareness was good: more than half — 53% — state that they would buy food preserved by radiation. Only 11% said flatly that they would not. When explanations and reassurances were added to the consumers' knowledge, about 82% appeared to accept the concept (Table 1). Resistance is concentrated in older women from families with lower incomes and less education. Of those consumers familiar with radiation processing, 33% had heard about it on television, 25% from magazines, and 16% from newspapers. Receptivity appears to be greater in the West; marketers already know the West as a precursor area. The consumers were provided with information on FDA approval, safety, taste, preparation, storage, availability, public information programs, and consumer benefits of radiation processed food. Afterward, 57% of the consumers said they would eat irradiated food; 17% said they definitely would not eat irradiated food. At the end of the briefing session, the consumers were asked to place themselves in one of four categories: 29% said they would try irradiated food without hesitation, 53% said they would try it eventually, 10% said they doubted they would try it, and only 6% said they would definitely not try it.

Table 1 CONSUMER ATTITUDES TOWARD IRRADIATED FOOD

	Those claiming familiarity* with "radiation processing," %		
	Have understanding, %	Have no or incorrect understanding, %	Total sample, after exposure to some facts about radiation processing, %
Yes (would eat)	72	46	57
No (would not eat)	8	12	17
Not sure	20	42	26

*Although 24% of the total claimed familiarity, only 6% of the total correctly understood the process. The remainder — 18% of the total — did not understand the process correctly.

CONSUMER ATTITUDES TOWARD LABELS ON IRRADIATED FOOD

Two separate research methods were used to evaluate seven label phrases. Some questions were answered on the national survey, and 106 women answered more questions after viewing displays in a store replica. The seven label phrases were: treated with ionizing radiation; treated with ionizing energy; processed with ionizing radiation; processed with ionizing energy; irradiated; pasteurized with ionizing radiation; and pasteurized with ionizing energy. The women agreed that *treated* and *processed* were familiar words, but none knew what they meant exactly. Several women claimed that *treated* was a method that made undesirable food more desirable. The word *pasteurized* was familiar to the consumers, meaning heating, sterilizing, or purifying. The consumers accepted *energy*, although they associated it with vitamins, health, or the sun's rays. *Ionizing* was the most unfamiliar word; only a few women connected it with atomic energy. The word that was most frightening and that produced agitation and apprehension was *radiation*. *Irradiation* was a suspect and frightening word, too, but not so much as *radiation*. About a dozen women defined *irradiation* as the process by which radiation was removed from contaminated food to make the food edible.

The label thought most descriptive was *pasteurized with ionizing radiation*, but *processed* and *pasteurized with ionizing energy* were thought to be the most positive labels. Yankelovich concluded that *pasteurized with ionizing energy* represents the best balance between immediate appeal and descriptive power. (Editor's Note: A recent FDA decision on labeling has

ruled out the use of *pasteurized*. Irradiated foods are *processed* or *treated*; the use of *ionizing* instead of the specific kind of radiation is allowed.)

Trade Attitudes

Is there a significant degree of apprehension about the use of radiation with food products among trade personnel that might negate the positive aspects of the process? Analysis of 310 meetings with supermarket chain executives, individual independent and chain-store managers, and institution and restaurant personnel clearly indicates not. Table 2 presents the results of the meetings. A number of those opposed to radiation treatment of food were generally antagonistic to any tampering with the "purity" of food; they spoke of contamination dangers that cannot be accurately measured yet. Those executives who have experience with or knowledge of radiation are among the most favorable toward irradiation of food. In summary, 91% of food-industry management personnel would go along to some degree or other if food irradiation is approved by FDA. In the discussions, about 36% of the group brought up consumer attitudes, but most of those who did so believed that the consumer will accept irradiated foods as safe if they are approved by FDA.

Product Analyses

Positive benefits and commercial incentives to innovate with radiation processing appear most promising for New England finfish. The prospects for Hawaiian papayas also appear to be promising, but the incentive to commercialize is not as great and benefits would not become apparent as soon as with the fish product. Despite the obvious technical benefits of radiation processing for Hawaiian mangoes and for Dungeness crab, market supply and industry considerations rule out any possibility of commercializing radiation processing of these foods. The technical advantages of radiation processing of bananas are not justified economically, and, since the king crab industry is based on canning and freezing, there are no benefits of any sort to be gained by irradiation of the product. A detailed presentation of the findings for each food follows.

NEW ENGLAND FINFISH

Seven facets of fish marketing were investigated: consumers' buying practices and attitudes toward more fresh fish, especially in inland markets; retailers' problems of spoilage losses, short buying, present marketing radius for fresh fish, and need for extended shelf life; attitude of restaurant management; attitude of institutional food servers; source of leadership in developing markets for irradiated fish; the fish industry's structure in regard to the feasibility of using radiation; and an accurate estimate of tangible economic benefits to be derived from irradiation of fish.

Consumers in three regions of the United States were interviewed to provide data for comparisons of seafood buying behavior and attitudes. The majority of those consumers serving fish meals are not aware of any shortage of fresh ocean fish. Consumption of fresh fish is heavier in coastal regions, of course. Only 6% of the households in the United States never serve fish, and 86% serve fish more often than once a month. However, when housewives in the survey were asked if there was anything that would make them serve seafood more often, the most frequent response —52%— was "nothing." Since irradiated fish will be marketed as fresh fish, housewives were asked how often they served fresh fish. In the Midwest, only 20% said they served fresh fish, and 40% of those serve it less than once a month. Reactions to availability of fresh fish varied. In the Midwest, 17% of the housewives said they would not switch to fresh fish if frozen fish continued to be available. However, an equal amount said they would serve fish more often, and 25% said they would serve a greater variety al-

Table 2 TRADE ATTITUDES TOWARD RADIATION

Attitudes	Total, % 310 in group	Local fish retailers, % 71 in group	Local fruit retailers, % 75 in group	Chain fish buyers, No.* 17 in group	Chain fruit buyers, No.* 20 in group	Institution personnel, % 40 in group	Restaurant personnel, % 87 in group
No fear of radiation	8	1	6	1	3	15	10
Acceptance dependent on FDA approval	46	48	35	8	8	48	53
Fear radiation	9	13	11	-	-	2	10
No comment on safety of irradiation (aided and unaided)	37	38	48	8	9	35	27

* Base is too small to be shown as a percentage (25 or less); therefore numbers are shown.

though not a greater amount of fresh fish. The percentages were only slightly different elsewhere in the nation.

Based on the survey, two assumptions regarding inland demand for fresh irradiated fish can be made: (1) One-third of inland consumers who now most often buy frozen fish will switch to irradiated fresh fish. (2) More optimistically, inland per capita consumption of fresh fish would rise to equal present coastal per capita consumption. On the basis of the first assumption, inland consumption of fresh fish would increase from 27 to 62 million lb, based on the population in 1965. On the basis of the optimistic assumption, inland consumption would rise to 95 million lb of irradiated fresh fish. Such a growth would occur primarily to the detriment of the frozen fish industry. The four New England finfish considered in this report — cod, haddock, sole, and flounder — account for about 13% of the fresh fish marketed.

Managers of retail fish departments reported an average 4% spoilage loss for fresh fish. Minor losses in distribution are about 1%. Trade personnel indicate that difficulty in judging freshness of fish contributes to these losses. Realistically, then, spoilage losses were assumed to be cut only 2.5% by use of radiation. A common practice of retailers is short buying; this means buying less than they think they can sell so that they run out before the fresh fish has time to spoil, forcing some consumers to substitute some other food for the fresh fish they intended to buy. For estimating the additional sales of fresh fish that might result from eliminating this practice, the nominal value of 10% was chosen. There was little disagreement with this figure by management personnel. As before, more purchases of fresh fish would probably decrease sales of frozen fish.

The marketing radius of fresh fish is limited at present to the distance a truck can reach in 24 to 30 hr — about 800 miles. The average purchase of fresh fish by retailers in the United States was reported to be 856 lb/month. Average retail shelf life reported was 3 to 4 days. A shelf-life extension of 2 weeks could open up a considerable inland market for fresh fish.

A basic assumption of the study was that irradiated foods would always be shipped by the least expensive means. To ship a box of 100 lb of fish from New England to Chicago by truck costs $13.44; to airfreight it costs $17.18. Several airline companies anticipate rate reductions of 10 to 30% in the next few years; a reduction of 30% would make airfreight competitive with trucking.

There seemed to be little agreement in the industry as to whether sale of fresh or frozen fish was more profitable. Nationally, 42% thought fresh fish offered more profit, and 45% thought frozen fish was more profitable. However, this decision is dependent on shipping costs and spoilage. In particular areas, lowering shipping costs and minimizing spoilage will make fresh ocean fish much more profitable than frozen fish.

Eleven of the 18 major chain-store buyers interviewed believe that irradiated fish will become a staple item once FDA approval is given. Moreover, 13 of the 18 felt that it will reach its potential within 5 years after it is introduced on the market. Most buyers felt that prepared fish products — fish sticks, for instance — would not be affected by greater purchases of fresh fish.

Restaurant managers' attitudes differ markedly from those of grocers. If fresh fish could be made available, 67% of the managers said this is what they would prefer to serve. The four most important considerations about fish for restaurants are taste, availability, profitability, and spoilage. Radiation processed fish already has superior taste; it can certainly meet the other three requirements. The extra holding time of irradiated fish was considered so valuable that 34% of the managers said they would be willing to pay 5 cents or more a pound as a premium.

Institutional organizations expressed enthusiasm for irradiated fish. They generally use frozen fish, though. After a briefing on irradiated fish, 20 of 33 managers of institutions interviewed were either very enthusiastic or positive about the advantages of radiation processing.

Discussions with local fish retailers, department managers for chains, and restaurant and institution buyers indicated that the major retail chains will probably have to take the lead in promoting irradiation of fish. Most of the chain buyers agreed; however, they expressed some reservations. They were very specific about stating that they do not wish to get involved in the actual development of a product of this type. Since expansion of the market and greater profits will also benefit the processors and since everything except the actual sale to the consumer is handled by the processor, the processor should take the lead in product development.

The New England fishing industry is one of the oldest enterprises in the United States. It is made up of small, nonintegrated companies — boat owners, processor–wholesalers, and distributors. There are fewer than half a dozen large comprehensive companies. However, a few important firms will move quickly to market irradiated fish once FDA approval is given.

New England finfish is sold at dockside auction except for that landed by vessels owned, leased, or contracted by large companies. Prices vary widely. Retailers reported more consistent costs — cod at 40 to 49 cents/lb and haddock at 45 to 55 cents/lb. They sell the four species at prices that vary from 69 cents/lb up.

This study assumed a dock price of 12 cents/lb for haddock; retail costs were assumed to be 46.3 cents/lb, including freight, for the New England area. Retail costs would be higher outside New England. The value

added by elimination of spoilage is 1.85 cents/lb when fish retails for 74 cents/lb; value added by substitution of fresh fish for frozen fish was estimated at 12 cents/lb. The most relevant consideration in a cost-benefit analysis is the extra profit that can presumably result; this was placed at 5 cents/lb. After all factors have been considered, Yankelovich concludes that benefits outweigh radiation processing costs by roughly 14 to 1.

HAWAIIAN PAPAYAS

The chances that irradiation of papayas will prove commercially feasible are far from certain. Realistically, the exotic papaya can only approach the volume of sales achieved by California avocados and fresh Hawaiian pineapples — not the volume of bananas or citrus fruits. Commercialization chances would be greatly improved by sufficient shelf-life extension to permit ocean shipment rather than air shipment.

The present volume of papaya sales is about 5 million lb; this contrasts to sales of 10 billion lb of oranges. In 1959, only four specialty stores on the West Coast carried papayas regularly; in 1965, over 140 carried papayas on a day-to-day basis. The decisive breakthrough in 1961 that led to greater consumption and sale of papayas was the switching to airfreight shipment because a shipping strike was in progress. The annual rate of growth of the market has averaged about 16%. A recent publicity program by both private industry and the state of Hawaii is spending about $60,000/year on promoting the sale of papayas. Three assumptions of the cost-benefit analysis were that historical growth of mainland demand will be maintained, that about one-fourth of the Islands' production will be a minimum amount available for sale, and that the maximum sale of papayas will reach the same level as that of California avocados.

The importance of lower price to papaya's long-range commercial prospects, whether irradiated or not, cannot be overemphasized. Papayas usually cost about 49 cents per fruit and serve two people; avocados sell from 13 to 39 cents apiece and usually serve several people. Consumers who now buy papayas reported that they would buy considerably more often if the price were 10 to 30 cents lower. Of the 20 produce managers interviewed, all but 4 favored price reduction over shelf-life extension as a means of increasing papaya sales.

The papaya is inexpensive to produce. Growers can make a small profit on sale at 4 cents/lb, and prices received by farmers on Hawaii in 1964 were up to 5.3 cents/lb. The price to retailers in San Francisco averaged $3.20 per 10-lb case in 1965. A full one-third of the difference comes from airfreight costs. If shelf life could be extended, advantage could be taken of surface shipment rates. For shipments of 15,000 lb, air cargo costs 6 cents/lb, and surface, about 2.25 cents/lb.

The salable life of papayas is too short to make ocean shipping a practical alternative to airfreight at present. Generally 5 to 10 days are available between picking and consuming papayas; papaya display time in stores averages 5 days. If irradiation can extend shelf life sufficiently to permit surface shipment, retail costs would drop about 30%. However, irradiation has so far resulted in an extension of only 3 days at practical doses (75 krads). Irradiation cost can vary from 9.4 cents/case, for ^{60}Co at 33 cents/curie and a throughput of 50 million lb/year, to 29.8 cents/case, for ^{60}Co at 70 cents/curie and a throughput of 5 million lb/year. Papayas would seem ideal for a radiation processing plant since the fruit is grown commercially year-round only in the Puna District of Hawaii, which means that one central facility could be kept busy all year.

The minimum effect of radiation processing would extend shelf life 3 days, reduce retail spoilage losses 17 to 30 cents/case, cost from 7 to 25 cents/case, and probably have little effect on consumer prices. The maximum effect would extend shelf life 8 days, reduce shipping costs 85 to 92 cents/case, cost from 7 to 25 cents/case, and probably result in significant consumer price reduction. The minimum effect suggests a break-even return on AEC investment; the maximum effect suggests a considerable benefit from AEC investment.

HAWAIIAN MANGOES

Hawaiian mangoes are the only product in this study that requires radiation processing as a prerequisite for marketing on the mainland. Mangoes are infested with a seed weevil that can be controlled by irradiation at 25 to 75 krads; fumigation is effective as far as the weevil is concerned, but the mango has to be cut open to be fumigated, which is very detrimental to mango keeping qualities. Prospective benefits from sale of mangoes would probably be offset by lower sales of other soft fruits.

The mango has not developed into a commercial fruit in the Hawaiian Islands because the fruit is readily available in everyone's backyard. Until the quarantine on mainland shipments is lifted, a commercial development is unlikely. If large-scale commercialization of mangoes does occur, it will probably happen beyond the cutoff date of this study — 1980. A mango market already exists in the United States, and as many mainland consumers have already eaten Florida mangoes as have eaten papayas. The mainland demand for Hawaiian mangoes could probably be developed as rapidly as supplies permit over the next 20 years or so. Benefits from investment of AEC funds in radiation commercialization for Hawaiian mangoes should probably be best viewed as spillover benefits accruing from establishment of the commercial feasibility of the more immediately obvious product — papayas.

WEST COAST CRAB

Prospects for radiation processing of Dungeness crab and Alaskan king crab are poor, although strong interest in extending the shelf life of Dungeness crab has been shown by industry. Landings of Dungeness crab vary; the recent trend is downward, supposedly because of a biological cycle. The Dungeness crab industry is scattered widely—from Kodiak, Alaska, to San Francisco, Calif. The season for landing Dungeness crab lasts only 6 months. In summary, a relatively small and uncertain volume is landed at widely dispersed points only half the year. The benefits from radiation processing are far below the costs of irradiation of Dungeness crab.

For Alaskan king crab, the situation is reversed but the results are the same. The market is relatively large—126 million lb was landed in 1965. There are only four large processors, all located in Kodiak, Alaska. The drawback is that the industry is not at all interested in irradiating king crab. The crab keeps excellently in either canned or frozen form; as a result, supplies and prices are stable. There is no need for radiation processing.

BANANAS

Bananas do not appear to need the benefits of radiation processing, although irradiation treatment of bananas is certainly technologically feasible. Research at the University of California, Davis, under Dr. E. C. Maxie has proven that 35 krads administered to Gros Michel bananas at color stage 1 or 2 delays ripening as much as 15 days if the fruit is kept at 53°F. Recently, research has been started on the Variety bananas (Valery, Lacatan, and Cavendish). Results indicate that 35 krads given to Variety bananas when green causes a ripening delay of 3 to 8 days.

The domestic banana industry is dominated by two large corporations that control over 80% of the market. Almost 95% of the bananas imported to the United States come from Honduras, Costa Rica, Panama, and Ecuador. Banana consumption per capita in the United States averages between 15 and 22 lb. Bananas are produced constantly by the plant; so there is no seasonal variation in supply or price. Although the Gros Michel banana was the predominant banana grown in 1960, the shift is toward the Variety bananas because they are resistant to Panama Disease. By 1970, about 85% of Central American acreage will be producing Variety bananas. The banana handling process is efficient and speedy; engineering studies by the major companies have shown that it is more economical to pay overtime than it is to construct refrigerated warehouses. The total handling process is continuous day and night, starting on any day of the week, depending upon the arrival of the banana boat. An average boatload will be 100 thousand boxes weighing about 42 lb apiece. When the bananas are unloaded in the United States, the receiver immediately places them in a ripening room and starts the ethylene gas treatment under controlled temperature and humidity conditions.

The two principal goals in banana marketing are to deliver as much high quality green fruit as possible and to sell as much of the boatload as possible before the boat docks. In 1965, at least 50% of the boatload was sold before docking about 60% of the time, and, between 20 and 30% of the time, the entire boatload was sold before it left the tropical port. Spoilage is kept at a minimum by speed and efficiency; the entire banana industry paid claims on approximately 0.5% of total sales in 1965. At the retail level, less than 8% of sales are lost by spoilage. Extension of shelf life would allow the retailer to order about 8% less fruit than he orders now. The retailers view radiation processing as a benefit, then, while the importers view it as a detriment since it would mean 8% less sales for them.

Alternative methods of preservation have been investigated by industry. Primarily, these are controlled atmosphere procedures and packaging modifications. Both methods are considered too expensive for domestic shipments. For European shipments, controlled atmosphere will probably cost 30 to 40 cents/box; irradiation will cost 25 to 32 cents/box. Cost data on packaging modifications, which are very promising, remain proprietary.

The need for any preservation method on domestic shipments is so small that industry sees little practical application of any method. This, of course, includes radiation processing.

Cost-Benefit Estimates

Extensive analyses of costs and benefits of radiation processing were undertaken for New England finfish, Hawaiian papayas, and bananas. Bananas were discussed in detail because they are the only product in the study that has a large, well-established market and is produced and marketed year-round in sufficient volume in concentrated areas to efficiently use radiation processing. The criterions that bananas fail to meet are those related to the size and value of loss caused by spoilage. Daniel Yankelovich, Inc., took the position that only tangible benefits—meaning those capable of accurate estimation—would be counted as gains from investment of AEC funds, although intangible benefits were acknowledged. If gains in sales of one food occur at the expense of other foods, the tangible benefits are considered to be nil.

Three benefits were identified for commercialization of radiation processing of New England finfish: expansion of an inland market, reduction of spoilage, and elimination of short buying. Under the first assumption, two estimates were made: The increase in sales could amount to that caused by consumers' changing to fresh fish from ocean fish, and the increase could amount to an increase in inland con-

sumption to match coastal consumption. The spoilage reduction was taken to be 2.5%; the change due to short buying would be a nominal 10%. In addition, FDA approval was assumed for 1967; a commercial facility was assumed to be on-stream by 1969; and a market buildup period of 4 years was allowed. Irradiation costs would vary between 1.56 and 1.25 cents/lb; additional shipping costs, i.e., inclusion of ice and larger package, were assumed to be twice that of shipping frozen fish. Total benefits were then estimated; under the lower increase assumption, benefits would reach $8.6 million, and under the higher increase assumption, benefits would reach $10.5 million. The AEC costs were concluded to be only $0.8 million; so the conclusion was reached that this program is well worth supporting in terms of net gain to the national economy.

Market assumptions for papayas are based on a minimum effect of an increase to 20 million lb sold on the mainland and on a maximum effect of 70 million lb by 1980. FDA approval is expected in 1967, and the Hawaiian Development Irradiator will stimulate commercial investment by 1969–1970. About 90% of the papayas will be irradiated; irradiation costs will vary from nearly 3 cents/lb in the early 1970's to just over 1 cent/lb by 1980. Irradiation processing costs will be partially offset by elimination of chemical fumigation. Minimum cost reduction will come from reducing retail spoilage by one-half; this is equivalent to about 2 cents/lb. The maximum effect will come from making surface shipment possible; this would amount to a reduction in cost of about 8.5 cents/lb. The result of these assumptions is a market benefit ranging from a minimum of $184 thousand to a maximum of $22.3 million. The AEC costs to achieve the market benefit will be about $670 thousand since the state of Hawaii and private industry are expected to assume development costs after 1970.

For bananas, demand is expected to grow in proportion to population. FDA approval is expected in late 1968 or early 1969; commercial investment and irradiators should be active by 1970–1972. After 1972, 90% of the bananas are assumed to be irradiated. Processing cost can vary from 0.42 cent/lb to 0.773 cent/lb, depending on ^{60}Co cost. Marketing benefits were estimated to be the reduction of present spoilage losses by 50% and by 25%. The worth of these benefits will range from $2 million to a cost-over-benefit margin of $118 million, i.e., a loss of $118 million. This does not include AEC costs, but they would be only about $100 thousand for the period 1967–1970. Commercial firms would pay for the rest of the development.

Recommendations and Conclusions

Daniel Yankelovich, Inc., described AEC's objective of commercialization of radiation processing as "obtuse" unless the concept of "commercialization" is brought down to the realities of industry. On a product-by-product basis, this is how Yankelovich defined commercialization:

1. New England finfish would be considered commercialized if a single major Boston processor and shipper began radiation processing of the product.

2. Papayas and mangoes would be considered successfully commercialized if the one or two fruit cooperatives and importers who account for virtually all mainland sales of these fruits began radiation processing.

3. Dungeness and Alaskan king crab will be commercialized if one or two leading packers of king crab adopt the process.

4. Bananas will be commercialized if both of the "big two" begin radiation processing.

The study points out that the present degree of commercial interest is too small to suggest that commercialization will result even if AEC stops support of the program; however, the study could find no real reason to expand AEC support of the program. Yankelovich recommended that serious consideration be given to instituting screening procedures to fully determine the real economic potentials of any radiation processing of foods. If only the three products on which they urge support to continue are brought to commercialization, they think AEC support more than vindicated. Yankelovich also mentions that, although irradiation of dehydrated soups was not on the list of materials to be studied, there was ample evidence in industry that this product will very likely be commercialized.

A publicity program to familiarize food editors of newspapers, magazines, and other mediums with radiation processing should be prepared. The facts of interest to consumers are that FDA approval is required before sale, that radiation treatment is not unlike other forms of treatment, and that radiation processed foods are stored and prepared just like fresh foods. All publicity should take into consideration that the consumer actually has neither positive nor negative attitudes toward radiation processing at this time.

The AEC's food-irradiation program has had a stronger research than marketing orientation. Yankelovich recommends that emphasis be shifted toward specific existing product needs. The market research effort required to develop product-need specifications is relatively small; the information can usually be acquired from three or four large processors and a similar number of large supermarket chains.

As a result of its cost-benefit analyses, Daniel Yankelovich, Inc., recommended that the AEC discontinue its research and development program on commercialization of radiation processing of Dungeness crab, Alaskan king crab, and bananas. The

program to commercialize radiation processing of New England finfish should be supported vigorously, the program on papayas should be supported at the same level as in the past, and the program on mangoes should be given marginal support by a program carried out in conjunction with that on papayas.

(F. E. McKinney)

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Design of the World's First Industrial-Scale Grain-Irradiation Facility

Abstract: The design of the world's first industrial-scale (50 tons/hr) grain irradiator—completed Feb. 1, 1967—is described here.

It has been estimated that insect infestation is responsible for the loss of approximately 5% of the world's grain supply, and even greater losses in nutritional value because the insects eat the most nutritious parts of the grain. Effective methods of insect control are necessary not only to prevent loss of food but also to keep food clean and pure and to prevent the spread of insects by international trade. Ionizing radiation has been shown to be a promising new tool for insect control.

The world's first industrial-scale grain-irradiation plant, having been constructed and tested for performance, was accepted by the client in February 1967 (Refs. 1 and 2). The project was initially conceived by 25 experts who attended a panel on Radiation Disinfestation of Grain held on May 21–24, 1962, at the Headquarters of the International Atomic Energy Agency (IAEA) in Vienna.[3-5] It was the recommendation of this panel that both a ^{60}Co and an electron accelerator plant be constructed, preferably at seaport silo installations (where existing or projected elevators could be used), and a further recommendation by this panel led to the submission, and ultimately the approval, of the wheat petition in the United States.

The IAEA delegates sent to Pakistan, Turkey, and Argentina, at the request of the respective governments, decided that the grain-handling and grain-trading conditions, as well as the incidence of infestation, in Iskenderun, Turkey, were sufficient justification for the installation of a plant. The khapra beetle, which is particularly difficult to eradicate by insecticides and fumigants, is prevalent in Iskenderun, and virtually all Turkish exports of grain go through this port.

Insects can be killed or sexually sterilized by radiation. Since sterilization accomplishes the same end as killing and the dose required is considerably lower, sterilization was chosen as the treatment. The insect eggs present in the food product are made infertile,[6] and the sterilized insects, which may live for several weeks after irradiation, offer a degree of protection, during this period, against reinfestations by the same species of insect. No protection is given against infestation by an insect species not already present in the grain.

Nuclear Chemical Plant Limited (NCP) of London, England, was awarded the contract for the construction of this Turkish ^{60}Co facility, and the discussion that follows is a description based on a paper by B. D. Baines, Irradiation Plant Manager, NCP, entitled "The Design of Plant for Grain Irradiation Including the Design of the World's First Continuous Grain Irradiator."*

Irradiation Facility

The irradiation facility is designed to handle wheat, barley, rye, and maize at a maximum rate of 50 tons/hr, the yearly average of the Iskenderun installation throughput. Although the maximum source capacity is approximately 360 thousand curies of ^{60}Co, 160 to 170 thousand curies will be sufficient to treat the maximum design throughput. The Atomic Energy Research Establishment, Harwell, England, supplied 100 thousand curies of ^{60}Co to the irradiation unit during February to treat 30 tons/hr (Refs. 7 to 9). Annual shipments of approximately 20 thousand curies will be necessary to maintain the same activity.

The irradiation facility, which was constructed adjacent to the existing silo installation, is a 100-ft concrete tower with the irradiation plant at the lower level and two 125-ton feed hoppers at the upper level (Figs. 1 and 2). The unirradiated grain is transported from the silo to the feed hoppers by a system of chutes, sieves, and conveyors and flows by gravity through a series of annular channels past the ^{60}Co source. The irradiated grain is returned to the

*Presented at Nuclex 66 International Technical Meeting, International Nuclear Industries Fair and Technical Meetings, September 8–14, 1966, Basel, Switzerland.

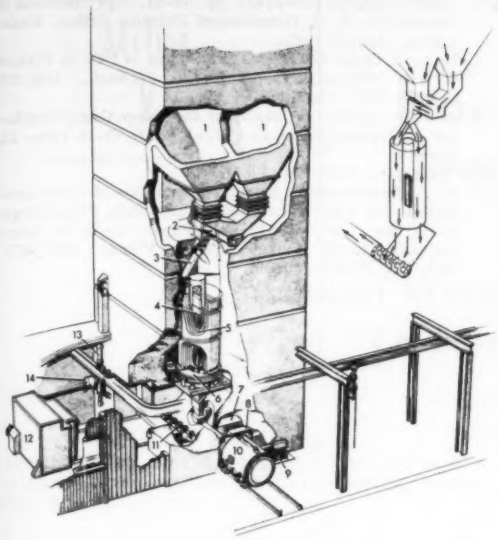

Fig. 1. Section through grain irradiator. 1, Feed hoppers (total capacity 250 tons); 2, feed conveyor; 3, grain ducts; 4, source plaque; 5, annular grain channels; 6, grain-flow regulator; 7, source-plaque storage container; 8, static storage container (optional); 9, static storage controls and interlocks; 10, transport container; 11, discharge conveyor; 12, plug door; 13, hydraulic cylinder; 14, regulator drive mechanism.

Fig. 2 World's first industrial-scale grain irradiator, Iskenderun, Turkey.

silo installation by conveyors, making the grain-irradiation facility continuous.

Grain is a very inhomogeneous material, and an accurately controlled flow—economically desirable to obtain a uniform dose throughout the grain[10] and to eliminate the waste of energy incurred in giving some of the material being irradiated a dose greater than the minimum necessary—is not obtainable with a variable-aperture-type flow-control device. A grain-flow-control device with volume flow independent of the grain or its flow characteristics but dependent only on controllable factors of the device itself was developed. The flow-control device consists of a flat, horizontal plate with a series of curved scoops, each adapted to an appropriate channel. Rotation of the plate results in each scoop moving through the grain and allowing a known volume to be fed from the channel. The rate of flow from the annular channels is controlled by the rotating scoops, each of which is individually set in accordance with the initial dosimetry tests. Each annular channel width is of adequate size to prevent any form of blockage; tests and calculations by NCP and United Kingdom Atomic Energy Authority, Wantage Research Laboratories, ensure a minimum-to-maximum dose ratio of within ±20% of the desired value. The overall throughput, however, is controlled by varying the speed of rotation of the flow-control device.

Cobalt-60 in the form of 12 pencils, each measuring 0.45 in. in diameter and 6.26 in. in length and containing 100 g of ^{60}Co (total, 1.2 kg), is loaded into each 12-in.-long Wantage source rod, and the rods are loaded from a source transport container into the source plaque. The source plaque is stored in a cell-floor pit, which is constructed of mild steel with an interlining of stainless steel. When the source is stored, this shielding is sufficient to reduce the radiation level in the cell above the storage pit to <0.75 mr/hr. The radiation level outside the building is 0.25 mr/hr during operation. The air that is drawn through the pit to cool the source is sampled for radioactivity, and this air-cooling system is supplemented by a thermosiphon system capable of cooling a source with a total strength >100 thousand curies.

Minimum costs for a cobalt plant are $0.21 and $0.12 per ton for throughputs of 50 and 150 tons per hour, respectively, for 6000 hr of plant operation per year.

Hopefully, Turkey will be the second country in the world to give clearance to irradiated grain for human consumption, now that the construction of the $1.8 million plant is complete. (Joan E. Carden)

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Section V

Isotopes and Radiation Technology

Process Radiation Development

Ethicon Worldwide Complex of ^{60}Co Sterilization Units

By Charles Artandi*

Abstract: The six Ethicon ^{60}Co sterilization facilities, in five countries, are described and the significant differences among them pointed out.

Five operating plants and one under construction make up the unusual collection of radiation sterilization units considered as the Ethicon complex. Three significant facts that may account for this abundance are: (1) the unique suitability of sutures for this type of processing; (2) the high degree of sterility ensurance required for the product; and (3) the willingness of a company, a worldwide leader in its field, to change existing packaging and sterilization technology and to explore uncharted waters. Experimental work begun in 1953 led to the use of electron accelerators for commercial-scale radiation sterilization of sutures at our Somerville, N. J., plant in 1956. The first ^{60}Co plant within the Johnson & Johnson family of companies, built by H. S. Marsh Ltd., was put in operation in 1961 by Johnson's Ethical Plastics Company in Slough, Buckinghamshire, England.

The first of the six plants in the Ethicon ^{60}Co pharmaceutical sterilization complex (Table 1) was that of our Scottish affiliate, Ethicon, Ltd., in Edinburgh. When they began to plan for the use of radiation sterilization, we jointly decided that a ^{60}Co plant would be more economical because it does not require the highly trained technical personnel who are essential for the operation of an accelerator installation. Their ^{60}Co plant, built by Nuclear Chemical Plant Ltd., was started up in 1962.

In 1964 Ethicon put in operation two plants in the United States and one in Canada, all three having been designed and built by Atomic Energy of Canada Ltd. (AECL). The fifth unit was completed in our Hamburg plant, Ethicon G.m.b.H., in 1966 by H. S. Marsh Ltd. The sixth unit, now under construction for our Italian plant outside Rome, is being built by AECL.

*Ethicon, Inc., Somerville, N. J.

The decision on the size and type of plant to be constructed is not an easy one. Many factors—present needs, potential growth, operating cost, prestige, and, to some extent, even national pride—may play an important role.

The selection of the designer is equally difficult and was more so some years ago when there were hardly any radiation plants from which performance characteristics could be evaluated. Radiation technology can become sophisticated only if all companies learn from the design and experience of all others in the field. And, when the decision has been reached to build a plant, one firm should be able to handle design, construction, installation, and shakedown operations (the "turn-key" concept). This new technology, in spite of its simplicity, is a puzzling one for people who have had no experience with radiation, and having to deal with several companies makes things too complicated.

There are proponents of both wet and dry source storage, and numerous points are raised by the designers—for one, or against the other. Many of these points represent an emotional approach to a logical problem. Experience has been showing that both systems are good and reliable if the people who design them are competent. When the designer has been selected, the storage system may have been automatically selected, although some firms are competent in both designs.

Before setting capacity requirements, one has to establish the packing density or range of packing densities of the products that will be irradiated. The packing density and the thickness of the product containers through which the radiation must penetrate determine, for a fixed conveyor speed, the amount of radiation absorbed in one pass. The efficiency of radiation absorption is influenced by

1. Overlap of the source by the product in the horizontal and vertical directions
2. Packing density (g/cm^3 or lb/cu ft)

3. Container thickness
4. Number of passes on each side of source
5. Dose uniformity requirements
6. Amount of "shine-through" where no radiation absorber is present
7. Amount of metal used in the conveyor system that holds and carries the product around the source

on the relation: 1,000,000 curies at 100% efficiency ≈ 11,700 Mrad-lb/hr radiation output. When the materials are of uniformly high density, multiple passes may result in efficiencies as high as 40 to 50%. Most of the time not all the requirements are met, and practical efficiencies fall in the range 5 to 30%, depending on the plant design.

Table 1 PLANTS IN THE ETHICON ^{60}Co STERILIZATION COMPLEX

Location	Company	Builder	Activity, curies: Total capacity	Activity, curies: Present charge	Source storage	Operation
Edinburgh, Scotland	Ethicon, Ltd.	Nuclear Chemical Plant Ltd.	250,000	84,000	Dry	Automatic
Somerville, N. J.	Ethicon, Inc.	AECL	750,000 to 1,500,000	450,000	Wet	Automatic
San Angelo, Texas	Ethicon, Inc.	AECL	750,000 to 1,500,000	80,000	Wet	Automatic
Peterborough, Ontario, Canada	Ethicon Sutures, Ltd.	AECL	100,000	30,000	Dry	Batch*
Hamburg, Germany	Ethicon G.m.b.H.	H. S. Marsh Ltd.	750,000	60,000	Dry	Automatic
Rome, Italy	Ethicon, S.p.A.	AECL	100,000	Under construction	Wet	Batch*

*Can be converted to fully automatic.

Many of these factors are interdependent, and what is good for efficiency may be bad for dose uniformity. All factors must be considered and a compromise made in order to achieve overall optimum conditions.

The purpose of all radiation processing is to expose a product to a predetermined nominal dose, which, in practice, is the minimum that will do the desired job. Dose uniformity is defined as the ratio of minimum dose to maximum dose, which ideally should be 1. On the other hand, the nature of the product (its radiation sensitivity) and the efficiency of the process (cost) determine how close the maximum and minimum doses are to each other. The dose uniformity of most processes falls in the range 1/1.2 to 1/1.5. It is determined by (1) packing density in relation to thickness of product container, (2) amount of product–source overlap, and (3) range of product densities.

Capacity requirements are generally expressed in megarad-pounds per hour. This may be the best unit for food and chemical products but is certainly not the best for most of the pharmaceutical and medical products. Since the products are not sold by the pound but by the number of units, the weight is meaningful only in establishing the packing densities of the various products. When these are known and taken into consideration in the design of the process, it is more convenient to use megarad-cubic feet per hour.

Product densities range from 0.1 to 0.8 g/cm^3, with most medical products falling in the range 0.1 to 0.4 g/cm^3.

The efficiency, i.e., the radiation used at the nominal (minimum) dose expressed as the percentage of the total available for absorption, is based

Description of Facilities

ETHICON, LTD., SCOTLAND

The design[1] of the Edinburgh unit differs significantly from that of all others because it uses a vertical chain conveyor (Lindstaedt elevator) system (Fig. 1). Two metal boxes, which hang freely on each of the horizontal steel rods that connect the chains at appropriate distances, are loaded with material to be sterilized and placed on the feed conveyor outside the cell. This high-speed monorail conveyor carries the unirradiated boxes to the vertical conveyor. At intervals the vertical conveyor stops, and a sterilized box coming from the cell is removed from the right side and placed on the high-speed monorail conveyor for removal. A box on the left side of the elevator is automatically moved to the right, a new box is placed in the vacant left-side position, and the cycle continues.

The vertical conveyor makes four passes, two on each side of the source. Each box makes four vertical passes—two on each side of the source—in the left-side position and is then transferred horizontally to the right side, where it makes another four vertical passes. The horizontal transfer is needed to even out the dose since the two boxes overlap the source in width. Because the boxes hang freely, they maintain their position throughout their passes and changes in the direction of travel at top and bottom of the elevator. Except for the stops for package transfer, the vertical conveyor is in constant, uniform motion.

The source is of the standard Wantage-tube type. It is loaded through the cell wall into the source-rack tubes and is stored dry in a cooled concrete pit below the floor of the cell when not in use.

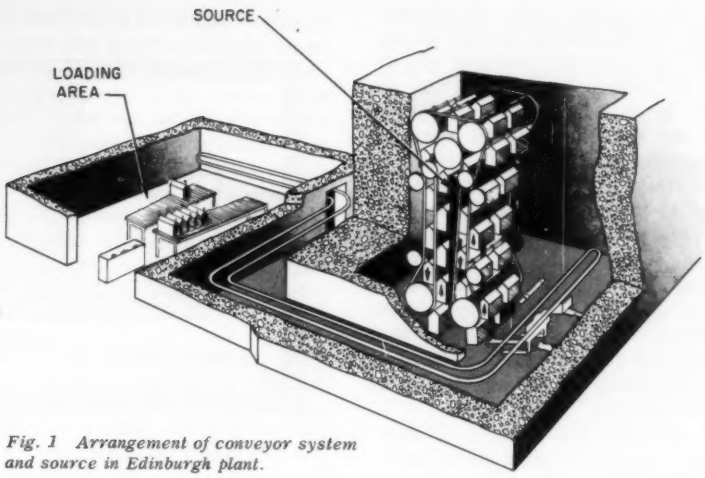

Fig. 1 Arrangement of conveyor system and source in Edinburgh plant.

ETHICON, INC., NEW JERSEY AND TEXAS

The New Jersey and Texas plants are identical in design,[2] and there are only two significant differences in the finished plants: The Texas unit is built completely underground, as is the main manufacturing plant to which it is attached, and its cobalt, about a fifth of that of the New Jersey unit, is distributed in only half of the source plaque. In 1966 a third pass was added to each side of the source conveyor at the New Jersey plant to further improve efficiency, but for the Texas plant the expense of this change is not justified at the present scale of operation.

The conveyor system (Fig. 2) consists of three parts: (1) load–unload station, (2) maze conveyor, and (3) cell conveyor. The product boxes are moved

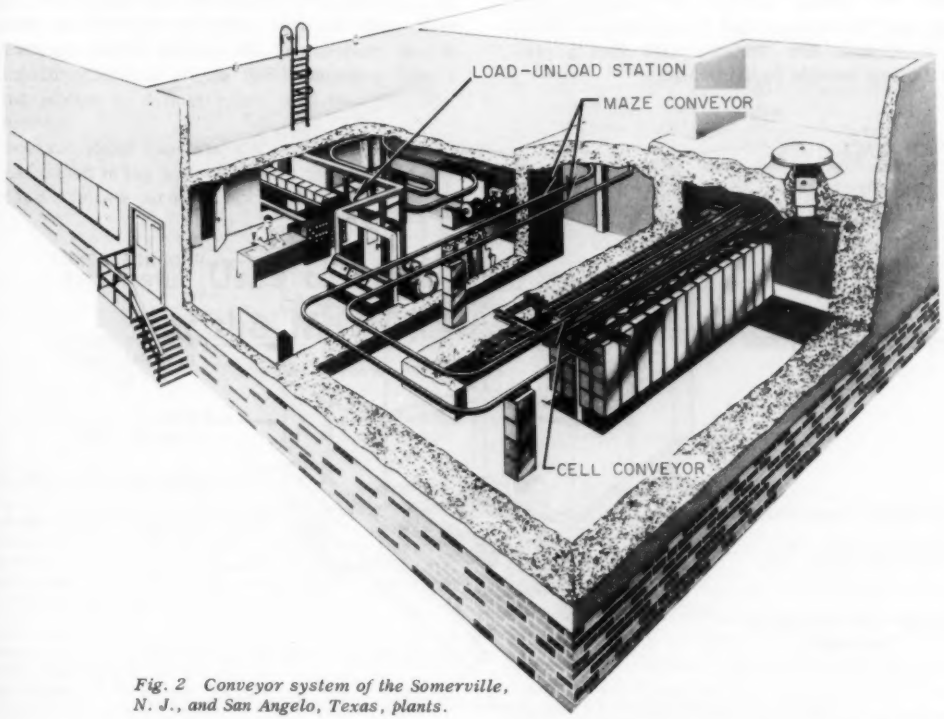

Fig. 2 Conveyor system of the Somerville, N. J., and San Angelo, Texas, plants.

through the system in a metal frame, or carrier, which has four open compartments on top of one another. At the load–unload station, which is outside the radiation cell, the boxes are handled with an elevator mechanism. In each cycle two irradiated boxes coming from the cell are removed from the two lower compartments (3 and 4) of the carrier. The boxes from the two top compartments (1 and 2) are then transferred to the two lower ones, and two unirradiated boxes are placed in the top compartments.

The top of the carrier is attached to a trolley head, which is taken, by an overhead chain conveyor from the load–unload station, through the maze and deposited in front of the cell conveyor system. Here it is picked up and taken through the cell and then back to the load–unload station.

The carriers are advanced and transferred from one pass to the next by pneumatic push and transfer devices located at both ends of the cell conveyor system. Motion is intermittent, and the steps are in predetermined sequence. Failure of completion of one cycle automatically aborts the next.

ETHICON SUTURES, LTD., CANADA, AND ETHICON, S.p.A., ITALY

The Canadian and Italian plant designs are the same. The Canadian unit (Fig. 3) started as a batch process[3] in 1964. The source is the double-squirrel-cage type. For source storage the Canadian plant uses a pit, and the source must be returned to Ottawa for replenishment. The Italian plant has a pool, which will allow on-site replenishment.

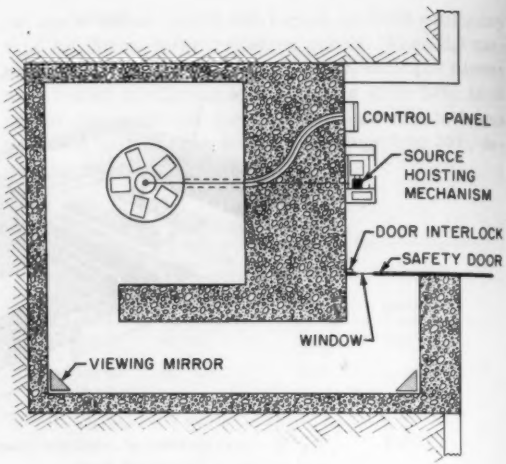

Fig. 3 Irradiator chamber of the Canadian and Italian plants.

The cell conveyor originally consisted of five slowly rotating turntables set in a circle around the source. Each turntable held two product boxes, one on top of the other, for a total of 10 boxes. At half the full processing time, the two boxes on each turntable were exchanged to ensure a uniform radiation dose.

For greater efficiency in use of radiation and for the possibility of complete automation, the cell conveyor was recently redesigned so that the irradiator is now loaded with 21 product boxes, i.e., stacks of 3 in 7 positions (Fig. 4). An eighth position allows

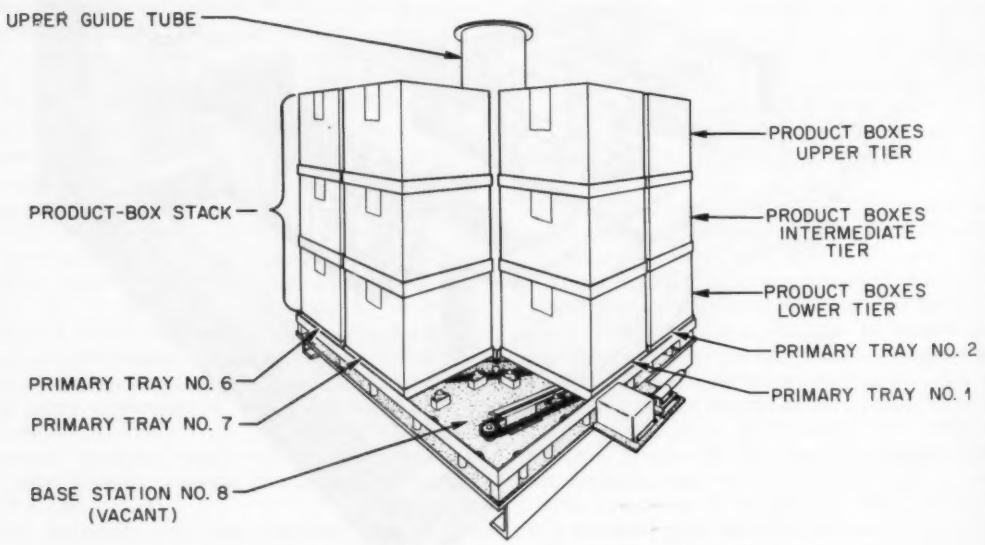

Fig. 4 New design of source-pass mechanism for the Canadian and Italian plants.

periodic, sequential shuffling of the stacks to expose all four sides of each box for the same length of time. When a third of the processing time has passed, boxes are removed from the top level. Boxes from the middle are moved to the top, and those from the bottom are moved to the middle. Fresh boxes are placed on the bottom. After each third of the radiation processing time, this sequence is repeated so that each box spends a third of the time at each level to ensure dose uniformity. This new unit is being installed in both the Canadian and Italian plants.

ETHICON G.m.b.H., GERMANY

In the German plant[4,5] the product, which is placed on metal carrier frames (four boxes high, individually separated) and suspended on roller trolleys from a fixed track, is moved by a chain conveyor through the radiation plant. The carriers enter the cell through a narrow maze on the left side and exit through an identical maze on the right side (Fig. 5). The product-box transfer device (load–unload station) is in front of the cell.

When a carrier arrives from the cell at the load–unload station, the completely irradiated bottom box (No. 4) is removed, boxes 1, 2, and 3 are shifted downward into positions 2, 3, and 4, and a fresh box is inserted in position 1. After each four passes around the source—two on each side—this operation is repeated at the load–unload station. Inside the cell, at the end of each pass around the source, the carrier is moved on a short movable track, which swings automatically 90° to engage and lock to the beginning of the next pass. The swing-arm self-returning motion is synchronized with the cell conveyor motion.

The source, which consists of the standard Wantage tubes, is housed in the source frame. It is stored dry in a cooled concrete pit when not in use.

A 10-ton manually operated plug door provides access to the cell. Controls are located on the same side of the cell as the plug door. (MG)

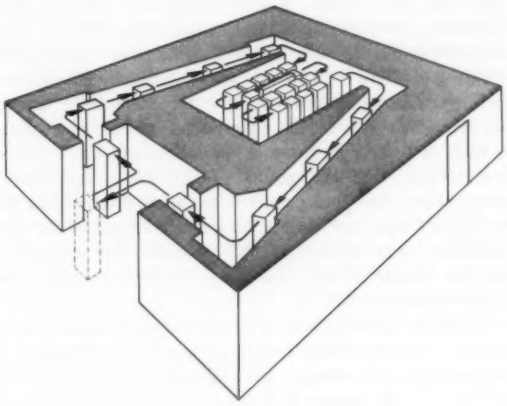

Fig. 5 Product flow path in the Hamburg Ethicon plant.

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Uses of High-Energy Radiation for the Modification of Textile Fibers

(A Review of the Literature 1963–1966)

By R. D. Gilbert* and V. Stannett†

Abstract: The literature from January 1963 to August 1966 on the use of radiation to modify textile fibers is reviewed. Degradation, cross-linking, and graft copolymerization are discussed, with emphasis on the use of graft copolymerization to modify properties of polyamide, polyester, celluosic, polyolefin, wool, and silk textile fibers. Some related ESR studies are also presented.

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Work on the effect of high-energy radiation on polymers[92] was initiated as early as 1929; however, extensive research has only been under way for about 15 years. In particular, the possibility of inducing desirable changes directly in textile fibers with radiation has attracted the attention of many researchers. The breaking of a chemical bond with high-energy radiation takes at least 10 ev and usually much more. This means that at least $\frac{1}{4}$ kw-hr of energy is needed to process 1 gram mole of material

if no chain reactions are involved, which is quite uneconomical for low-molecular-weight material. However, since textile fibers are composed of molecules of extremely high molecular weight, a large amount of material can be processed per kilowatt-hour on the basis of one molecular change per molecule even without chain reactions. This is the economic basis, for example, for the successful commercial process of radiation-induced cross-linking of polyethylene and for the suggested use of radiation for controlled reductions in the molecular weight of high polymers. In radiation-induced polymerization, whether actually graft or in situ polymerization, the chain nature of the reaction leads to the highly efficient use of the energy required for the initiation step itself. In other words, the high molecular weight of the resulting polymer provides an amplification factor.

A useful quantitative relation for calculating such energy requirements has been given by Restaino[115] as: number of pounds per kilowatt-hour = $8.23 \times 10^{-4} \times G \times M$, where G is the G value for the overall reaction (number of molecular events for 100 ev of absorbed radiation) and M is the molecular weight of the molecular unit involved.

The main changes brought about in textile fibers by high-energy radiation are basically of only three types. These are degradation or chain breaking, cross-linking—either direct or via additives, and grafting including in situ polymerization. These effects are reviewed and the recent literature in the field is summarized. The number of publications in this general field is large, and *only material published from January 1963 to August 1966* will be specifically mentioned.

The changes brought about by irradiation nearly always proceed via a free-radical mechanism, although ionic reactions can be induced under special conditions. There has been increasing use of electron spin resonance (ESR) for measuring and attempting to identify the radicals involved in radiation treatments. A brief review of this aspect of the work, as directly related to textile fibers, is presented at the end of this article.

There have been several reviews of the modification of natural and synthetic fibers and polymers by radiation, including two recent ones by Schwarz[120] and Morris,[91] and an interesting earlier one by Roberts.[116] Stannett[125] and Krassig and Stannett[71] reviewed the radiation-induced graft polymerization of various monomers to cellulose and its derivatives, including grafting procedures, extent of grafting, characterization of the grafts, and the properties; Holm[45] reviewed the radiation-induced graft copolymerization of cellulose; Livshits and Rogovin[81] have reviewed through 1964 the various methods, including radiation initiation, of preparing graft copolymers of cellulose and its derivatives. The application of high-energy radiation in textile research was discussed by Stannett,[126] and the use of radioactive isotopes in textile research and technology was the subject of a recent symposium.[90] The application of nuclear radiation to textile materials and processes was reviewed by Armstrong and Rutherford[3] at the Symposium on Industrial Uses of Large Radiation Sources, at Salzburg, Austria. Schurz[119] recently concluded that there is much detailed information on how to graft-copolymerize various monomers onto various substrates by radiation initiation but that as yet there has been no technical exploitation of this knowledge. However, there have been recent announcements[144] regarding a successful radiation process for durable press fabrics. Other encouraging notes may be found, for example, in the work of Das Gupta[40] who was sufficiently encouraged by preliminary work to scale up the process of grafting methyl methacrylate to cotton for the evaluation of larger fabric samples. Blouin, Morris, and Arthur[22] appeared confident that a number of desirable properties could be introduced into grafted fibers by the proper selection of monomers and conditions and methods of grafting.

Degradation and Cross-Linking

Extensive studies of the effect of high-energy radiation on polymers in the solid state have been under way for many years. Useful reviews of the earlier work may be found in the monographs of Bovey,[26] Charlesby,[29] and Chapiro.[28] Regardless of the initial species produced, the results of irradiation have been interpreted by most researchers in terms of free radicals produced by the radiation. Important exceptions, however, exist—particularly in the case of polyethylene—where ionic intermediates have been suggested, most recently, for example, by Libby[79] and by Kevan and Libby.[64,65] The polymeric radicals may either combine, which leads to cross-links, or disproportionate, which leads to chain cleavage, i.e., degradation. With many polymers both processes occur, and the resultant properties depend on the balance of the two effects. Attempts have been made to correlate the type of behavior with the heat of polymerization and other factors; these approaches are discussed by Bovey[26] and Chapiro.[28] In general, the overall effect of the radiation is clear-cut, and polymers can be classified as degrading or cross-linking types. However, there are polymers—notably polyvinyl alcohol and polyethylene terephthalate—for which reports are still somewhat conflicting. The effect of radiation may be drastically changed by variations in the temperature and the dose rate and by the presence or absence of oxygen. Degradation is usually highly favored by the presence of oxygen; however, many textile fibers are sufficiently crystalline for this effect to be minimized by the slow rate of diffusion of oxygen to the active centers. A review of the effect of radiation on some solid polymers may be found in

the recent papers of Schwarz[120,121] and Morris[91] and in the earlier papers of Bobeth, Heger, and Weihs.[23,24] The effect of radiation on the mechanical and electrical properties of some 45 polymers was summarized by Pascale, Herrmann, and Miner.[99] Types of polymers examined included polyethylene, polypropylene, polyamides, polyesters, polymethyl methacrylate, and cellulose esters. Polyethylene was among the least affected, while acrylics and the cellulosics were most affected.

EFFECTS OF RADIATION ON TEXTILE FIBERS

In addition to these more general studies of degradation and cross-linking, there have been a considerable number of papers specifically dealing with the effects of radiation on various textile fibers. For convenience, references to specific fibers are given in Table 1.

Armstrong, Walsh, and Rutherford[4] studied the rates at which the physical properties of a number of fibers were changed by gamma radiation. The predominant effect was degradation; some of the fibers degraded faster in the presence of oxygen. Bobeth et al.[25] exposed polyamide, polyacrylonitrile, polyester, cuprammonium rayon, and flax fibers to various doses of neutrons and gamma radiation and examined changes in tensile and elongation properties, swelling, solubility, and structure. Polyacrylonitrile and polyesters had the highest and flax the lowest overall resistance to radiation. The data of Fomenko et al.[34] indicated a high radiation stability for polyamides.

According to Arthur and Blouin,[8,20] irradiation of cotton cellulose produces long-lived free radicals that exist in significant concentrations for periods lasting up to 20 days and possibly longer. These long-lived free radicals exist in the crystalline

Table 1 EFFECT OF HIGH-ENERGY RADIATION ON VARIOUS FIBERS

Fiber type	Radiation source	Remarks	Refs.
Cellulose (cotton)	^{60}Co	Study of types of radicals formed	14, 15
Cellulose (cotton)	^{60}Co	ESR study of radical types	33
Cellulose	^{60}Co	ESR study of radical yields	35
Cellulose (cotton)	^{60}Co	ESR study	73
Cellulose	^{60}Co	ESR study	6
Polyamide		ESR study; kinetics of radical decay	70
Polyamide		ESR study	89
Polyester	^{60}Co	ESR study of radicals in amorphous and crystalline regions	5
Polyamide Polyethylene Polyvinyl alcohol	^{60}Co	Cross-linking studies	16, 17
Polyamide Polyethylene Polypropylene Cellulose acetate		Summary of effect of high-energy radiation on mechanical properties	99
Polyamide Polyester Acrylic Rayon Flax	Reactor, ^{60}Co	Effect on physical properties	25
Polyamides	^{60}Co	Aromatic polyamides have high radiation resistance	34
Polyethylene	^{60}Co	Morphological study	67
Polyamide	^{60}Co	Deformability study	1
Polyester	^{60}Co	Gas and carboxyl group yields	27
Polypropylene	^{60}Co	Effect on interfacial electrical properties	137
Polypropylene	^{60}Co	Effect of N_2O on cross-linking	61
Polyamide Polyester Polypropylene	^{60}Co	Changes in physical properties	4
Acrylic Cellulose (cotton, rayon) Cellulose acetate	^{60}Co	Changes in physical properties	4
Cellulose (cotton)	Linear accelerator	Study of long-lived free radicals	8, 20
Cellulose (cotton)	^{60}Co	Effect of low doses on physical properties	20
Cellulose	^{60}Co	Chain cleavage studies; decomposition products identified	49
Cellulose	Reactor, ^{60}Co, cathode-ray tube	Depolymerization; decomposition products identified	53
Cellulose (cotton)	^{60}Co	Cross-linking	145
Cellulose	^{60}Co	Effect on dyeing	93
Cellulose (cotton)	^{60}Co	Degradation study	107
Cellulose	^{60}Co	Polymolecularity study	108
Cellulose (rayon)	^{60}Co	Inhibition of degradation studies	69
Cellulose (cotton)		Modification of fiber properties	97
Cellulose (cotton)	Thermal reactor	Strength-loss studies	110
Cellulose	^{60}Co	Effect on physical properties; detection of small amounts of radiation damage	130
Cellulose acetate	^{60}Co	Study of position of chain cleavage	147
Cellulose	^{60}Co	Degradation in air and N_2	68
Methyl cellulose	^{60}Co	Degradation study	21
Wool	^{60}Co	Radiation damage vs. dose level; effect on dyeing properties	47

regions, and, owing to the immobility of the chains, the free radicals are relatively immobilized and cannot readily react with other active species. No significant decrease in strength properties was found if the irradiation dosage was $<2.3 \times 10^6$ rads with ^{60}Co gamma radiation or with electrons from a 7-Mev linear accelerator operating at 2.80×10^6 rads/hr. A statistical analysis by Horio et al.[46] shows that there is no appreciable change in strength properties of wool fibers by irradiation with doses less than 10^7 rads and that radiation damage is statistically probable only at doses greater than 10^8 rads. Horio, Imamura, and Mizukami[48] found that chain cleavage of cellulose took place in proportion to $R^{0.85}$, where R is the radiation dose.

Imamura[53] states that the extent of rupture of irradiated cellulose molecules is directly proportional to the radiation intensity and that the damage is independent of the source. Both he and Horio et al.[48] detected the formation of aldehyde, ketone, carboxyl, formyl, and acetyl groups and the evolution of hydrogen as well as small amounts of CO, CO_2, and CH_4. Horio et al.[48] showed that the hydrolyzate of strongly irradiated cellulose contains an appreciable amount of xylose, arabinose, and glucuronic acid besides glucose—which suggests the transformation of carbohydrate components by the irradiation. The authors suggested that the rapid decrease in the leveling-off of the degree of polymerization (DP) indicates a likelihood that the cleavage took place equally in both the amorphous and crystalline domains. They also observed a crystallite size reduction with an electron microscope.

Apparently there is some confusion as to which domain is preferentially attacked (Refs. 16, 48, 52, 98, 107, 108), but the most definitive work is by Kitamaru and Mandelkern[67] who found that irradiation at different temperatures has a different effect on the amorphous and crystalline regions of polyethylene. At low temperatures there is essentially no difference in cross-linking efficiency between a highly crystalline specimen and one in which the crystallinity is not as well-developed. However, at temperatures sufficiently high for molecular motion of the chain units to occur, cross-linking is more easily accomplished in a highly crystalline specimen than in a completely amorphous one. According to computations by Spiro and Winkler,[123] to distinguish between cross-linking and end-linking as alternative mechanisms of radiation-induced network formation in high polymers should be possible by comparing gelling doses for samples of different initial distributions. They think this should be a useful technique for studying radiation processes in polymers that form networks, especially since this method is insensitive to degradation.

Klein and Tikomolova[69] found that α-methyl styrene and p-benzoquinone inhibited the degradation of viscose by reacting with the free radicals produced on cellulose by irradiation. Although the degradation decreased when the methanol solvent was freed of dissolved air, the products of methanol radiolysis promoted degradation, which could be of significance in any grafting experiment on rayon in a methanol medium. The work of Pedemonte et al.[100] on irradiation of polystyrene shows that there is a limiting molecular weight, M, below which the chain is not degraded and that MI = constant (where I is the intensity of radiation); this suggests a limit on the graft-branch chain length.

Polcin[108] examined the changes in chain-length distribution of cellulose during gamma irradiation and demonstrated that the long chains are attacked preferentially and that DP reductions are accompanied by a leveling-off in chain distribution. Pande[97] discussed the effect of nuclear radiation on the physical and chemical properties of the cellulose molecule and on the structure of cotton and its dyeing properties. He also discussed potential uses in finishing.

Raubenheimer and Galbraith[110] found that various vat dyes did not catalyze the oxidative reaction of cotton caused by gamma rays and may even have offered slight protection. They found only slight losses in the yarn strength. Sulser, Mohler, and Luethy[130] claim dyeing cellulose with basic and acid dyes is a very sensitive method of detecting the effects of radiation doses of the order of 10^6 rads, where chemical changes cannot be detected.

Wellons and Stannett[147] obtained G values for dry films of cellulose acetate irradiated by ^{60}Co in air and in vacuum, as well as in various solvents. They suggest that cleavage occurs after removal of a hydrogen atom at the 1, 4, or 5 position. In solution, cleavage may be forestalled by radical chain transfer to solvent molecules or by addition of monomer before cleavage can occur. Klein et al.[68] found that the amount of degradation of cellulose acetate is somewhat higher during irradiation in nitrogen than in air, and, as might be expected, air-dry samples are more resistant to radiation than samples containing 40 or 100% water.

Blouin et al.[21] showed that irradiation of methyl cellulose results in chain cleavage, demethylation, and the formation of carbonyl and acid groups, peroxides, and formaldehyde. After irradiation the concentration of acid groups decreased, but the chain length and carbonyl content remained constant.

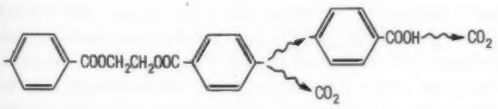
Sulser et al.[130] studied the effects of gamma radiation on water sorption, behavior towards H_2O, hydrolysis kinetics, and dyeing capacity of cellulose. Nitzl[93] attributed the decrease in the amount of acid dye and the increase in amount of basic dye absorbed by cellulose, as the radiation dose increased, to increases in carboxyl-group content.

Horio et al.[47] found that, although the rates of dye absorption of wool are significantly decreased by low irradiation doses, the mechanical properties are not changed. At higher doses the wool fibers regain dye

accessibility. At a 10^6-rad dose the strength properties—tensile strength, elongation at break, and Young's modulus—are greatly affected, but absorption of dyes becomes even greater than that of unirradiated fibers. To explain these observations, Horio et al. propose that two parallel effects occur in wool during irradiation. The first effect, manifested by decreased dye accessibility and decreased solubility at low doses (10^3 to 10^5 rads), suggests cross-linking; the remarkable increase in dye uptake at higher doses is associated with the second effect—a high degree of fiber structural damage.

Irradiation of polypropylene fibers in air or water has a strong influence on their interfacial electrical behavior, and infrared absorption spectrums show that negative dissociation groups are formed.[137] Karpov et al.[61] compared the effect of N_2O on the radiation cross-linking of polyethylene and polypropylene. The cross-linking of polyethylene is higher in the presence of N_2O than in vacuo up to doses of 150 Mrads; at higher doses the gel content reaches a limiting value that is independent of the presence of N_2O. The gel content of polypropylene is lower in vacuo at all doses, the limiting value being 70 to 75% in vacuum and 85% in N_2O. The deformability of films of mixed polyamide resins at temperatures above the melting point decreased with increasing irradiation,[1] suggesting cross-linking.

The primary effect of gamma radiation on polyethylene terephthalate appears to be degradation. The rate of formation of carboxyl groups at low doses is much too high to fit the simple reaction scheme:



but a better fit is obtained over a range of higher doses, about 100 to 5000 Mrads.[27]

Several studies have been made of cross-linking fiber entities using functional monomers and radiation. Walsh, Jin, and Armstrong[145] found *N*-methylol acrylamide to be a particularly versatile monomer in connection with cellulose, particularly from a "delayed cure" viewpoint, as it can be polymerized in the fabric at room temperature by radiation and the system later cross-linked by a chemical cure; the reverse was also studied. Very recently Rutherford and Walsh[117] have further investigated the process whereby the methylol acrylamide is first chemically linked to the cellulose. In a later step, cross-links were introduced by radiation, presumably through the vinyl group. Even polymers that degrade with radiation can be cross-linked by radiation using difunctional vinyl monomers such as allyl methacrylate and triallyl cyanurate. This extremely interesting method was first introduced by Pinner and coworkers[103–106] to effect radiation cross-linking of polymers that normally degrade. The efficiency of cross-linking of polymers that normally do cross-link was later found to be greatly enhanced by this technique. Armstrong, Walsh, and Rutherford[4] found that the dose necessary to cross-link nylon-66 sufficiently to resist melting at 290°C was reduced from 50 Mrads to only 1 Mrad in the presence of 1.9% allyl methacrylate.

Bernstein and coworkers[16,17] cross-linked nylon and polyvinyl alcohol by irradiation in allyl methacrylate, and polyethylene by irradiation in divinyl benzene, allyl methacrylate, and diallyl maleate; using this technique, they were able to cross-link nylon and polyvinyl alcohol at low radiation doses where there is an insignificant amount of degradation.

Graft Copolymerization

Papers on radiation-induced graft copolymerization of many different vinyl monomers with polymer fibers constitute by far the largest volume of the publications surveyed in this review. This interest has been comparatively recent. During the period 1953 to 1958, most radiation chemistry studies were directed toward the effects of radiation on solid polymers and polymerization per se. Since then, however, interest in radiation grafting has become widespread. The reason for this interest is the intriguing possibility of modifying polymers to obtain new and interesting properties leading to better performance.

Graft copolymerization is different from random or block copolymerization in that it usually leaves the main polymeric substrate backbone essentially intact. Thus grafting, as a rule, can be expected to add the new and additional properties associated with the side chains without drastically changing the main properties of the substrate. This is particularly interesting in textile fibers, which owe their existence to the symmetry and regularity of their molecular architecture. To disturb this symmetry with copolymerization in the main chain would lead, for example, to lower elastic modulus and melting or softening points. Grafting, however, within fairly broad limits, does not bring about such changes. In fact, surprise is often expressed at how little the properties are affected by substantial degrees of grafting. Therefore additional properties may be built into fibers without drastically changing their overall performance. This fact is not generally appreciated, and many vain attempts have been made to improve by graft polymerization the overall performance of fibers with respect, for instance, to their mechanical behavior.

Properties which can, in principle, be readily built into a fiber by radiation grafting include dyeability, antistatic properties, and oil- and dirt-release qualities. There are probably many more such examples.

The considerations that determine commercialization are mainly economic; the lack of understanding of the feasibility of radiation processing and the pressure of effective competitive chemical processes are also drawbacks.

There are a number of elementary considerations that are often overlooked. For example, in a fiber grafted with 10% of a given monomer, the molecular weights of the side chains are normally extremely high because of the gel effect, i.e., the delayed chain-termination reaction in the swollen fiber. As a result, typical side-chain molecular weights could be close to 10^6. The molecular weight of the fiber polymer on the other hand is often many times less. Consequently, with a 10% graft, only a very small proportion of the fiber molecules is grafted. Actual analyses of model grafting systems[124,147,149] have confirmed these considerations. Many workers in graft copolymerization believe that many short side chains would be preferable to a few long ones for the development of useful properties. However, this normally would lead to lower G values; i.e., a much larger total dose would be needed to effect the same amount of grafting. This means much higher radiation costs; the grafting may also be accompanied by undesirable side effects. One method of achieving more numerous side chains having lower molecular weights would be by the addition of chain-transfer agents; some work along these lines has been reported by Hayakawa, Kawase, and Matsuda.[42] However, such a method would usually be expected to lead to a large excess of occluded homopolymer.

The case of grafting to wool was unusual; many short chains were grafted[128] with such a high G value for chain initiation that there must have been considerable chain transfer to the fiber itself.

What differences in behavior might be expected between occluded polymer and actual grafted polymer for textile fibers is not clear. Probably the only real difference would be in permanence, i.e., perhaps there would be a slow migration or demixing in the case of occluded polymer.

There are three main methods of radiation grafting; these are the mutual, preirradiation, and peroxide methods. The *mutual* technique involves irradiating in the presence of monomer either in the liquid or vapor phase. The method is limited, in general, to systems where the radical yield from the substrate polymer is higher than that from the monomer; otherwise excessive homopolymerization results. For textile fibers, monomer may be padded onto the fibers and then irradiated. The *preirradiation* method involves irradiating the polymer alone and then bringing it in contact with either liquid or gaseous monomers. The grafting takes place by the reaction of the monomer with the trapped radicals. Virtually any monomer can be grafted by this technique. The *peroxide* method involves irradiating the polymer in air and later decomposing the resulting polymeric peroxides in monomer. Both the mutual and the peroxide methods lead also to homopolymer, whereas the preirradiation method leads mainly to true graft copolymer. In practice, the preirradiation and peroxide methods can be combined and the eventual grafting brought about by a mixture of trapped radicals and peroxide decomposition.

The importance of diffusion in the grafting process has been discussed in detail by Chapiro.[28] There must be sufficient monomer available at the active centers produced by the irradiation to initiate sufficient chain formation before termination of the process. The practical results of this requirement are quite remarkable: to graft dry cotton, for example, is virtually impossible. The addition of a few percent of water, however, enables grafting to take place with ease, because the diffusion of monomer in moist cellulose is manyfold higher than that in the dry state. The same arguments apply both to vapor- and liquid-phase grafting. With hydrophobic fibers the monomer itself may swell the fiber sufficiently for rapid diffusion to the active centers. Details of studies on the role of diffusion in graft copolymerization may be found in the papers discussed in the literature section.

Closely allied to the problem of diffusion is the effect of dose rate on the grafting process. In mutual radiation grafting, the yields of graft are highly dependent on dose rate. At low dose rates there is ample time for monomer to diffuse in and grafting to take place before termination. At very high dose rates, however, the yields drop off greatly. There is nearly always some grafting, even at the highest dose rates such as from machine irradiation. Experiments have shown,[128] at least for wool, that most of this grafting occurs after irradiation because of the buildup of radicals during the radiation process. With the preirradiation and peroxide techniques, the dose rate is much less important, and even at very high dose rates adequate grafting can be achieved. Since the monomer must diffuse into the fiber from the outside, the diffusion control should lead to a greater concentration of graft at the surfaces. With the judicious selection of dose rates, swelling conditions, and time of contact with the monomer(s), locating the graft at various depths in the fiber, according to need, should be possible.

The grafting of a wide variety of vinyl monomers on the various fibers is summarized in Table 2, and the recent literature is discussed below according to fiber type.

POLYAMIDES

The kinetics of the radiation-induced graft copolymerization of acrylonitrile to nylon-6 (Kapron) fiber was examined by Kornev et al.[72] who found the rate could be represented by the equation

$$\frac{dk}{dt} = \frac{k_p C_m c}{(1 + k_0 ct)}$$

(Text continues on page 414.)

Table 2 RADIATION-INDUCED GRAFT COPOLYMERIZATION ON VARIOUS FIBERS

Fiber type	Monomer grafted	Monomer form	Radiation source	Refs.
		Polyamide Fibers		
Nylon-6 (Kapron)	Acetylene Acrylonitrile Acrylic acid Butadiene Ethylene Methyl methacrylic acid Phenyl acetylene Propargyl alcohol Propylene Styrene Vinyl acetate	Vapor phase	^{60}Co	143
Nylon-6 (Kapron)	Acrylonitrile Ethylene Methyl methacrylate Propylene	Vapor phase	X-ray source (80 kv, 200 ma)	134
Nylon-6	Vinyl pyrrolidone	-		132
Nylon-6 (Kapron)	Styrene	Vapor phase	^{60}Co	76
Nylon-6	Styrene	Vapor phase	^{60}Co	75
Nylon-6 (Kapron)	Acrylonitrile	-		77
Nylon-6	Acrylonitrile	-	^{60}Co	71
Nylon-66	Methacrylic acid	-	^{60}Co	84
Nylon-66	Acrylic acid Maleic acid	-	^{60}Co	82
Nylon-66	Acrylonitrile Butadiene Ethyl acrylate Methyl acrylate Vinyl acetate	Vapor phase	^{60}Co	2, 3 2 3
Nylon-66	Acrylic acid Acrylonitrile Allyl acrylate Butadiene 1,3-Butylene dimethacrylate Divinyl sulfone Ethylene Ethyl acrylate Ethylene dimethacrylate Methyl acrylate Methyl methacrylate Propylene Styrene Vinyl acetate Vinyl chloride *n*-Vinyl pyrrolidone Ethylene dimethacrylate–methyl acrylate Ethylene dimethacrylate–acrylic acid 1,3-Butylene dimethacrylate–acrylic acid	-	^{60}Co	4
		Polyester Fibers		
Polyethylene Terephthalate (Terylene)	4-Vinyl pyridine	-	^{60}Co	116, 150
Polyethylene Terephthalate	Methacrylic acid		^{60}Co	84
Polyethylene Terephthalate (Lavsan)	Styrene	-	^{60}Co	76
Polyester	Acrylic acid Acrylonitrile Butadiene Divinyl sulfone Ethyl acrylate Ethylene Methyl acrylate Methyl methacrylate	-	^{60}Co	4

Table 2 (Continued)

Fiber type	Monomer grafted	Monomer form	Radiation source	Refs.
	Propylene Styrene Vinyl acetate Vinyl chloride *n*-Vinyl pyrrolidone			
		Cellulose Fibers		
Cellulose	Methyl acrylate Methyl methacrylate Vinyl acetate	-	^{60}Co	11
Cellulose	Styrene	-	^{60}Co	14
Cellulose	Polyvinyl alcohol (vinyl acetate)	-		18, 19
Cellulose	Styrene	-	^{60}Co	63
Cellulose	Acrylonitrile Methacrylamide	-	^{60}Co	66
Cellulose	Methyl acrylate	-		80
Cellulose	Acrylonitrile Methyl acrylate Methyl methacrylate Styrene Vinyl acetate	-		88
Cellulose	Styrene	-	^{60}Co	96
Cellulose	Acrylonitrile–styrene Methyl methacrylate–styrene Methyl methacrylate–acrylonitrile Methyl methacrylate–α–methyl styrene Acrylonitrile–α–methyl styrene Vinyl acetate–styrene	-	^{60}Co	109
Cellulose	Methacrylic acid		^{60}Co	112
Cellulose (cotton)	Acrylonitrile Butadiene Ethyl acrylate Methyl acrylate Vinyl acetate	Vapor phase	^{60}Co	2, 3
Cellulose (cotton)	Acrylic acid Acrylonitrile Allyl acrylate Butadiene Divinyl sulfone Ethylene Ethyl acrylate Methyl acrylate Methyl methacrylate Propylene Methylol acrylamide Styrene Vinyl acetate Vinyl chloride *n*-Vinyl pyrrolidone	-	^{60}Co	4
Cellulose (cotton)	Acrylonitrile Styrene	-	^{60}Co	7, 8, 10, 20
Cellulose (cotton)	Styrene	Solution	^{60}Co	12
Cellulose (cotton)	Styrene	-	^{60}Co	15
Cellulose (cotton)	Acrylonitrile Methyl methacrylate Vinyl acetate	-		22
Cellulose (cotton)	Styrene	-		39
Cellulose (cotton)	Acrylonitrile Styrene Methyl methacrylate Styrene–acrylic acid Styrene–methyl methacrylate	-	^{60}Co	40

Table 2 (Continued)

Fiber type	Monomer grafted	Monomer form	Radiation source	Refs.
	Acrylonitrile–methyl methacrylate			
Cellulose (cotton)	Styrene	–	^{60}Co	50, 51
Cellulose (cotton)	Styrene	–		102
Cellulose (cotton)	Methacrylic acid	–	^{60}Co	111
Cellulose (cotton)	Methacrylamide Methyl acrylate	–	^{60}Co	113, 114
Cellulose (cotton)	Butadiene–styrene Butadiene–acrylonitrile Styrene–acrylonitrile Butadiene–styrene–acrylonitrile	–	^{60}Co	118
Cellulose (cotton)	Styrene	–		135
Cellulose (cotton)	Butadiene Butadiene–styrene Butadiene–acrylonitrile	–		136
Cellulose (cotton)	Acrylonitrile α-Methyl styrene Vinylidene chloride Vinyl toluene	–	^{60}Co	141
Cellulose (cotton)	Acrylonitrile Methacrylamide Methacrylic acid Methyl methacrylate Styrene	–	^{60}Co	142
Cellulose (cotton)	Acrylonitrile Butadiene Ethyl acrylate Methyl acrylate	–	^{60}Co	3
Cellulose (rayon)	Styrene	–	Atomic reactor	37
Cellulose (rayon)	Styrene	–	^{60}Co	50, 51
Cellulose (rayon)	Styrene Acrylonitrile	–	^{60}Co	54, 55, 56 56
Cellulose (rayon)	Styrene	–	^{60}Co	60
Cellulose (rayon)	Styrene	–	^{60}Co	63
Cellulose (rayon)	Styrene	–		85
Cellulose (rayon)	Styrene	–		101
Cellulose (rayon)	Styrene	–	^{60}Co	114
Cellulose (rayon)	Vinyl pyrrolidone	–	^{60}Co	132
Cellulose (rayon)	Butadiene Butadiene–styrene Butadiene–acrylonitrile	–		136
Cellulose (rayon)	Acrylic acid Acrylamide Allyl acrylate Butadiene 1,3-Butylene dimethacrylate Divinyl sulfone Ethylene Ethyl acrylate Ethylene dimethacrylate 2-Ethyl hexyl acrylate Methyl acrylate Methyl methacrylate Propylene Styrene	–	^{60}Co	4

Table 2 (Continued)

Fiber type	Monomer grafted	Monomer form	Radiation source	Refs.
	Vinyl acetate Vinyl chloride *n*-Vinyl pyrrolidone Allyl acrylate–acrylic acid 1,3-Butylene dimethacrylate–acrylic acid Ethylene dimethacrylate–acrylic acid Ethylene dimethacrylate–methyl acrylate			
Cellulose acetate	Acrylonitrile Butadiene	-	^{60}Co	3
Cellulose acetate	Styrene	-	^{60}Co	41, 42, 43, 44, 62
Cellulose acetate	Acrylic esters	-		52
Cellulose acetate	Styrene	-		87
Cellulose acetate	Acrylonitrile–styrene Methyl methacrylate–acrylonitrile Methyl methacrylate–styrene Vinyl acetate–styrene α-Methyl styrene–acrylonitrile α-Methyl styrene–methyl methacrylate	-	^{60}Co	109
Cellulose acetate	Styrene	-	^{60}Co	122
Cellulose acetate	Styrene	-	^{60}Co	124, 127, 146, 147, 149
Cellulose acetate	Styrene	-	^{60}Co	129
Cellulose acetate	Methyl methacrylate	-	^{60}Co	149
Cellulose acetate	Acrylic acid Acrylonitrile Allyl acrylate Butadiene 1,3-Butylene dimethacrylate Divinyl sulfone Ethylene Ethyl acrylate Ethylene dimethacrylate Methyl acrylate Methyl methacrylate Propylene Styrene Vinyl acetate Vinyl chloride *n*-Vinyl pyrrolidone Allyl acrylate–acrylic acid Ethylene dimethacrylate–acrylic acid 1,3-Butylene dimethacrylate–acrylic acid	-	^{60}Co	4
		Polyolefin Fibers		
Polyethylene	Styrene	-	^{60}Co	32, 58
Polyethylene	Butadiene	-	^{60}Co	36
Polyethylene	Vinyl chloride	-	^{60}Co	59
Polyethylene	Methyl methacrylate Styrene Vinylidene chloride Dichloroethylene Trichloroethylene Tetrachloroethylene	-	^{60}Co	59
Polyethylene	Acrylonitrile Ethylene	-	^{60}Co	134

Table 2 (Continued)

Fiber type	Monomer grafted	Monomer form	Radiation source	Refs.
	Methyl methacrylate Propylene			
Polyethylene	Methacrylic acid	-	^{60}Co	84
Polyethylene	Acrylic acid Acrylonitrile Acetylene Butadiene Ethylene Methyl methacrylate Phenyl acetylene Propylene Propargyl alcohol Propylene Styrene Vinyl acetate	-	^{60}Co	143
Polyethylene	Acrylic acid Acrylonitrile 2-Methyl-5-vinyl pyridine	-	^{60}Co	148
Polypropylene	Acrylonitrile Butadiene Ethyl acrylate	-	^{60}Co	2, 3
Polypropylene	Butadiene	-	^{60}Co	36, 58
Polypropylene	Acrylic acid Methyl methacrylate	-	^{60}Co	38
Polypropylene	Glycidyl methacrylate	-	^{60}Co	57
Polypropylene	Styrene	-	^{60}Co	86
Polypropylene	Acrylic acid	-	^{60}Co	94
Polypropylene		-	^{60}Co	95
Propylene	Vinyl pyrrolidone Vinyl acetate	-	^{60}Co	132, 133
Polypropylene	Acrylonitrile Ethylene Methyl methacrylate Propylene	-	^{60}Co	134
Polypropylene		-	Atomic reactor (n,α reaction used to produce α particles)	138, 139
Polypropylene	Styrene–maleic acid Styrene–fumaric acid Styrene–diethyl fumarate Styrene–itaconic anhydride Styrene–maleic anhydride Vinyl acetate–maleic anhydride Acrylonitrile–maleic anhydride 2-Methyl-5-vinyl pyridine–maleic anhydride	-	Atomic reactor (n,α reaction used to produce α particles)	140
Polypropylene	Acetylene Acrylic acid Acrylonitrile Butadiene Ethylene Methyl methacrylate Phenylacetylene Propargyl alcohol Propylene Styrene Vinyl acetate	-	^{60}Co	143
Polypropylene	Acrylic acid Acrylonitrile 2-Methyl-5-vinyl pyridine	-	^{60}Co	148
Polypropylene	Acrylic acid Allyl acrylate Butadiene 1,3-Butylene dimethacrylate Divinyl sulfone Ethylene Ethyl acrylate Ethylene dimethacrylate Methyl acrylate Methyl methacrylate	-	^{60}Co	4

Table 2 (Continued)

Fiber type	Monomer grafted	Monomer form	Radiation source	Refs.
	Propylene Styrene Vinyl acetate Vinyl chloride *n*-Vinyl pyrrolidone			
		Wool Fibers		
Wool	Acrylonitrile Butadiene	-	^{60}Co	3
Wool	Acrylonitrile Methyl methacrylate Styrene	-	^{60}Co	48
Wool	Acrylonitrile Allyl acetate Allyl benzoate Allyl stearate Styrene	-	^{60}Co	128
Wool	Acrylic acid Acrylonitrile Butadiene Divinyl sulfone Ethyl acrylate Ethylene Methyl acrylate Methyl methacrylate Propylene Vinyl acetate Vinyl chloride *n*-Vinyl pyrrolidone	-	^{60}Co	4
		Miscellaneous Fibers		
Polyvinyl chloride	Glycidyl methacrylate	-	^{60}Co	57
Polyvinyl chloride	4-Vinyl pyridine	-	^{60}Co	121
Jute	Styrene	-	^{60}Co	83
Cyanoethylated cotton	Acrylonitrile	-	^{60}Co	7
Acrylic	Methacrylic acid	-	^{60}Co	84
Acrylic	Acrylic acid Acrylonitrile Butadiene Divinyl sulfone Ethyl acrylate Ethylene Methyl acrylate Methyl methacrylate Propylene Vinyl acetate Vinyl chloride *n*-Vinyl pyrrolidone	-	^{60}Co	4

where k_p and k_0 are the rates of growth and breaking of chains, respectively, C_m is the concentration of the monomer at the fiber surface, and c is the initial concentration of free radicals on the surface of the filaments. Kurilenko et al.[76,77] showed that the rate of grafting styrene on nylon-6 (Kapron) is limited by the diffusion of styrene to the free radicals in the fiber. Ballantine and Glines[13] showed that the rate of grafting on nylon-66 is increased by solvents (chlorinated solvents also act as chain-limiting agents) but conclude that no mechanism is available which adequately explains the role played by all solvents.

Matsuda and Maeda[84] found that the amount of methacrylic acid grafted on nylon-66 is independent of irradiation temperature from –78 to +30°C and explain this on the basis that a trapped radical is difficult to form in nylon.

Armstrong, Walsh, and Rutherford[4] point out the significant role of the rate of diffusion of monomer and the kinetics of the reaction in the vapor-phase grafting of nylon and, indeed, of all polymers. Since both the rate of graft polymerization and location of the grafts markedly affect the copolymer properties, these workers emphasize the need for accurate diffusion and kinetic data to obtain optimal results.

Magat and coworkers[82] modified the properties of nylon-66 by grafting on maleic or acrylic acid, using a mutual radiation-grafting technique in which the fiber was irradiated while swollen. The graft copolymers showed marked differences from the original nylon in hydrophilic properties, melting point, and recovery properties. The sodium salts of the grafts were highly hydrophilic, and the fiber melting temperatures of the sodium and calcium salts were

raised from 240 to >350°C, depending upon the graft level. Fibers from the sodium salt grafts showed a high wet-crease recovery, which rose sharply with increased humidity. The grafting occurred mainly in the amorphous regions of the polyamide substrate, with few changes in crystallinity. As a result, tensile properties such as tenacity and stiffness, which are functions of the crystalline areas, were retained in the graft.

Kurilenko and coworkers[75] found that grafting of polystyrene modified the surface properties of polycaprolactam. At 1% polystyrene the wettability of the fibers increased, but at 2% it decreased. There was also a direct correlation between wettability and adhesion of the grafted fiber to a polyester resin. The growth of the side chain in the amorphous region caused a decrease in the orientation, breaking elongation, and diffusibility of nylon-6 fibers.[76]

Both Tsetlin[134] and Vlasov et al.[143] found that the fiber, if oriented, serves as a matrix for the graft polymer, inducing its orientation. Tsetlin also demonstrated that the graft copolymers on nylon possess independent mechanical strength since irradiation (80-kv, 200-ma X-ray source) in the absence of the gaseous monomers results in fiber degradation.

Rutherford and coworkers[2-4] did not find any marked changes in tensile properties of nylon-66 grafted with various amounts of acrylonitrile, butadiene, or ethyl or methyl acrylate. Styrene grafts improved the weathering resistance of nylon. Grafts of acrylic acid alone or in combination with cross-linking monomers such as allyl acrylate, ethylene dimethacrylate, or 1,3-butylene dimethacrylate increased the elastic modulus of nylon-66 but did not alter its creep characteristics.

POLYESTERS

The paucity of published information indicates that there is little interest in attempting to alter the properties of polyester fibers by radiation grafting. This is undoubtedly because polyesters show little tendency to undergo grafting owing to their high resistance to radiation.[3,4,25,84]

Zielinski and Achmatowicz[150] investigated the effect on dyeing with acidic dyes of grafting various vinyl monomers onto polyethylene terephthalate film. Kurilenko et al.[76] found that styrene side chains increased the orientation, breaking elongation, and diffusibility of polyethylene terephthalate (Lavsan) fibers in contrast to nylon-6 and explained the difference on the basis of the destruction of polyester fibers and the cross-linking of polyamide fibers.

CELLULOSIC FIBERS

As may be readily judged from Table 2, by far the greatest activity in radiation grafting has been concerned with cellulose in its various forms and derivatives. The rate and uniformity of grafting onto cellulose are influenced by the technique employed—vapor phase, monomer phase, or solution;[2-4,11,88] the degree of accessibility;[2-4] the nature of the monomer;[2-4,11] and the presence of "sensitizers"[2-4,11,14,74] or oxygen inhibitors.[4,96]

The grafting activity of cellulose decreases with increasing irradiation temperature, and grafting nardly occurs above 35°C according to Kimura and Okada.[74] However, the data of Rutherford and coworkers[3,4] show that cellulose acetate is the only fiber that exhibits a consistent relation between grafting and temperature, the degree of grafting decreasing over the range of 30 to 125°C; cotton and rayon exhibited various maximums and minimums—presumably as different effects became predominant.

Rapson and Kvasnicka[109] made an extensive study of grafting monomer mixtures onto cellulose. Acrylonitrile has a synergistic effect on the grafting of styrene onto cellulose. But with the combinations vinyl acetate–styrene, methyl methacrylate–styrene, and methyl methacrylate–acrylonitrile, addition of one monomer to the other caused an initial increase and then a continuous decrease in the extent of grafting. Alpha-methyl styrene did not graft (nor did it homopolymerize), but mixtures with acrylonitrile or methylmethacrylate did graft as did mixtures of butadiene, vinyl chloride, or vinyl acetate with styrene.

Livshits et al.[80] and Azizov, Usmanov, and Sadykov[11] grafted methyl acrylate onto cellulose. Azizov et al.[11] also examined the grafting of methyl methacrylate and vinyl acetate. They found the formation of the grafted copolymers was affected by the nature and concentration of the monomer and the nature of the solvent employed. The tensile strengths of the graft copolymers were not substantially different from cellulose, but the hydrophilic nature of the graft copolymers was lower.

Biber and Konkin[18,19] prepared grafted copolymers of polyvinyl alcohol and cellulose by first preparing polyvinyl acetate grafts followed by hydrolysis. They also prepared the xanthates of the grafted copolymers and found their solution viscosity to be substantially lower than the viscosity of cellulose xanthates. Khakimov, Usmanov, and Sadykov[68] investigated the water-vapor sorption and the integral heats of wetting (by H_2O) of polyacrylonitrile and polymethacrylamide graft copolymers. The results were higher or lower than for cellulose depending on the properties of the graft side chains. Arthur and coworkers[7,20,22] and Razikov and coworkers[111-114] have made extensive electron-microscope studies of the microstructure of a number of graft copolymers of cellulose.

Cotton. That the use of "sensitizers" such as water, methanol, acetic acid, and concentrated $ZnCl_2$ solutions accelerates the rate of grafting on cotton is well known (Refs. 2, 3, 7, 12, 15, 50). There seems no doubt that the major role played by these additives is to swell the fiber, leading to greatly increased rates of diffusion of the monomer and perhaps higher initial monomer concentrations in the fiber. In addition, the additives can participate in the grafting

process by forming free radicals by radiolysis and perhaps by other interactions. Some work[35] has been done on the location of the grafting sites, but no conclusive evidence seems to be available. Huang et al.[49] estimated that only one in 5 to 10 thousand anhydroglucose units, or one in 10 to 20 cellulose chains, carries a grafted polystyrene chain.

Rutherford and coworkers[3,4] and Usmanov[141] have studied the kinetics of vapor-phase grafting onto cotton. Arthur and coworkers[10,22] and Sakurada et al.[118] provide data on radiochemical yields of graft-polymerization reactions on cotton cellulose.

Rutherford and coworkers[3,4] and Huang and Rapson[50] describe direct radiation grafting onto cellulose cotton as a heterogeneous reaction in which monomer diffusion plays a key role and the extent of grafting is controlled by reaction variables such as preswelling and radiation dose. They both postulate that grafting only occurs in the amorphous (accessible) region. Kesting and Stannett[63] compared grafting onto cotton (high crystallinity) and cellophane (low crystallinity). They could explain all their results in terms of free-radical formation under the various irradiation conditions and the accessibility of the potential grafting sites on the cellulose chains.

Arthur and Daigle[9] found that the molecular weights of polystyrene, grafted by using the mutual radiation technique, varied between 3×10^5 and 6×10^5 depending on the dosage, which confirmed the results of Kesting and Stannett[63] and Huang et al.[49] However, using a postirradiation grafting technique, Blouin, Morris, and Arthur[22] obtained very high molecular weights—1 to 3×10^6.

Arthur, Markezich, and McSherry[7] showed that the structure of cotton fibers can be changed by the formation of graft copolymers with acrylonitrile and styrene, the polymers being located within the lumen and growth layers of the fibers. Blouin and Arthur,[20] using a postirradiation technique, found that acrylonitrile in concentrated aqueous $ZnCl_2$ solutions could penetrate the crystalline regions of cellulose. Such swelling agents cause the polymerization to start at the surface and work inward; in the absence of swelling, polymerization proceeds uniformly throughout the fiber. Blouin, Morris, and Arthur[22] extended the above-mentioned postirradiation technique to other monomers and found that, with methyl methacrylate as well as acrylonitrile, the reaction occurred predominantly in the outer cellulose layers of the cotton fiber structure, but with vinyl acetate the grafted polymer was uniformly distributed throughout the fiber cross section.

Electron-microscope studies by Razikov and coworkers[111–114] showed that methacrylic acid monomer penetrates not only into the free but also into the densely packed cellulose portions and causes a compaction of the supramolecular structure. It is probably responsible for the modified physical properties of the graft copolymer.[111,112] The width of the fibrillar formations in cotton cellulose and graft copolymers of methacrylamide and methyl acrylate were 100, 130, and 150 A, respectively;[113] this was explained by Razikov et al. on the basis of the different dimensions of the grafted molecules. They[114] found that methyl acrylate uniformly penetrates the various cellulose zones and that uniform grafting occurs throughout the entire fiber cross section.

Rutherford and coworkers[4] observed that the rate of grafting to cotton was increased by partial acetylation, hydroxyethylation, and cyanoethylation but that it was unaffected by partial methylation and carboxymethylation. Arthur, Markezich, and McSherry[7] grafted acrylonitrile onto cyanoethylated cotton and noted that the products were thermoplastic in nature.

According to Blouin, Morris, and Arthur,[22] the rate of the grafting reaction varies with the physical form of the cotton (fiber > yarn > fabric). The differences were attributed to physical restrictions on swelling introduced when the fibers are twisted into yarns and woven into fabrics. As may be noted in Table 2, just about every available vinyl monomer or mixture of monomers has been grafted to cotton cellulose using a variety of techniques and graft levels so that a wide range of properties has been observed. The interested reader is referred to the particular papers for exact details.

Rutherford and coworkers[2–4] found little change in the mechanical properties of cotton by grafting on of acrylonitrile and butadiene, ethyl acrylate, or vinyl acetate but did observe that cotton modified by the grafting of 3.5% acrylonitrile was almost immune to microorganism attack. Arthur, Markezich, and McSherry[7] found that acrylonitrile or styrene grafts on cellulose were thermoplastic, probably due to lowered cohesive forces on the cellulose, and showed decreases in resiliency index with increasing temperature. Azizov, Usmanov, and Dadykov[12] observed no noticeable change in the tensile strength of cotton fibers by grafting on of polystyrene, but the resistance to mineral acid was improved and the heats of wetting by water and the sorption of water vapor were reduced.

Blouin, Morris, and Arthur[22] found by postirradiation grafting of acrylonitrile, methyl methacrylate, or vinyl acetate in concentrated aqueous $ZnCl_2$ solutions that a wide range of graft copolymer contents could be attained at dosages low enough to avoid serious radiation damage. The grafted yarns were thermoplastic in nature and showed a marked increase in elongation at break and a decrease in stiffness. The acrylonitrile-grafted cotton had significantly improved rot resistance and markedly improved abrasion resistance. The polyvinyl-acetate-grafted cotton fabrics also exhibited marked improvement in abrasion resistance.

Das Gupta[39,40] reports that the physical properties of cotton grafted with acrylonitrile, styrene, methyl methacrylate, and mixtures of these monomers were greatly superior to those of her starting materials

as regards tensile strength, crease recovery, dye acceptability, and rot and water resistance. She performed some large-scale production runs using a pneumatic irradiation facility and obtained uniform grafting and duplication of the previously described desirable properties.

Pikler et al.[102] report improved mechanical properties as well as resistance to water penetration and to NaOH solutions by polystyrene grafts. Tsuji, Imai, and Kadono[135] report similar results.

Usmanov and Azizov[142] state that certain infrared bands may be used to determine the extent of grafting. They describe the properties of cotton grafted with methacrylic acid, methyl methacrylate, methacrylamide, acrylonitrile, or styrene and find that the tensile strength of cellulose fibers is unchanged by grafting, but that the thermal stability, resistance to microorganisms, adhesiveness, and dye affinity are increased. These results are similar to those of Rutherford and coworkers[3,4] for polyacrylonitrile grafts. The heat of wetting by water and water-vapor sorption may be either increased or decreased depending upon the nature of the grafted monomers and the methods and conditions of grafting.[58,142]

Sakurada et al.[118] have induced graft polymerization of acrylonitrile, butadiene, and styrene onto cotton in vacuo using a mutual irradiation technique with gamma rays from a ^{60}Co source or a preirradiation technique using a Van de Graaff accelerator. They obtained very high degrees of grafting by controlling the amount of swelling of the cotton and the radical formation. Usmanov[141] found that acrylonitrile grafts imparted resistance to bacterial attack but vinylidene chloride grafts reduced the resistance of cotton. He found vinyl toluene and α-methylstyrene to be very inefficient as grafting agents.

Armstrong, Walsh, and Rutherford[4] grafted allyl acrylate to cotton cloth and found improvements in both dry- and wet-crease recovery properties. Acrylic acid grafts provided improvements in wet- but not in dry-crease recovery, while grafts of methylol acrylamide followed by chemical curing improved dry-crease recovery but not wet-crease recovery properties.

Rayon. Gagnaire and Vincendon,[37] employing nuclear magnetic resonance, demonstrated that polystyrene, formed by irradiating styrene and viscose rayon in an atomic reactor, is chemically bound to the cellulose chains. Their data also indicated that polystyrene units, in which polymerization has been initiated by radicals formed on the cellulose, will react with neighboring cellulose chains without interrupting the growth of the chains.

Huang and Rapson[50] found that grafting of cellulose occurred readily only when the cellulose was preswollen with a polar swelling agent; they attributed differences observed in the grafting behavior of rayon and cotton to differences in fine structure. For rayon, grafting with styrene increased sharply after 30% water content, passed through a maximum at 60 to 80%, and then decreased. For cotton cellulose, grafting occurred after 10% water content, increased up to about 20%, and then remained constant. As noted previously, the postulated grafting takes place only in the amorphous, or accessible, regions.

Huang[51] studied grafting of rayon in bulk styrene and in styrene–solvent mixtures, such as styrene–methanol and styrene–acetone, and found that in bulk styrene the molecular weight of the grafted polystyrene ranged from 4×10^5 to 1×10^6, while the polystyrenes formed in the presence of the polar solvents were of the order of 3 to 5×10^4. The molecular weights of the grafts tended to increase with the degree of grafting and, further, their molecular weights decreased with increasing polar solvent content. These results are not unexpected in view of Huang and Rapson's observations noted above. Huang observed that carbon tetrachloride, a reasonably good chain-transfer agent, caused a sharp decrease in the graft-copolymer molecular weight. He also found that the solubility in cupriethylene diamine decreased and the equilibrium moisture content increased with grafting but that the hygroscopic nature of the cellulose portion of the grafted rayon did not change. This suggests that the amorphous regions of rayon remain relatively loose and permit water molecules to diffuse despite the presence of polystyrene.

Rutherford and coworkers[3,4] studied the effects of radiation on rayon and grafted a considerable number of monomers to this fiber but evidently found the difference between cotton and rayon not worthy of a separate discussion. Huang and Rapson[50] did not observe any significant changes in the mechanical properties of styrene-grafted rayon at high graft levels.

Employing a stained cross-section technique, Imamura and Taga[54] showed that a high level of styrene grafting occurs in the inner portions of viscose rayon fiber and a lower level in the skin areas. Imamura, Taga, and Inagaki[55] found by sedimentation studies four peaks in the molecular-weight-distribution curve of polystyrene grafts. Imamura and Washijima[56] found the degree of grafting of aqueous solutions of acrylonitrile proportional to the degree of swelling of the fiber. Photomicrographs and X-ray studies suggested that the grafted polyacrylonitrile is deposited in the amorphous regions of rayon and crystallized.

Kaeppner and Huang[60] grafted styrene onto three types of commercial rayon (Fortisan, high-tenacity tire yarn, and modifier-type, high-wet-modulus yarn). Electron photomicrographs indicated that the polystyrene was distributed throughout the cross section of the filament and also appeared on the surface of all three grafted fibers. As a result, the filaments expanded isometrically during grafting but retained their original shape. Kaeppner and Huang concluded that the bulk of the polystyrene was truly grafted to the cellulose chains and that from a macroscopic

viewpoint the styrene-grafted regions are homogeneous. On a molecular basis, however, they consist of a gross heterogeneous mixture of polystyrene homopolymer, cellulose, and cellulose–styrene graft copolymer.

Matsuda et al.[85] and Pikler et al.[101] also studied the modification of rayon by grafting polystyrene. Suzuki and Ogawa[131] found that reducing cations (Ti, Sn, Ni, Cr, or Co chlorides) accelerate the radiation grafting of styrene to rayon in aqueous solution, presumably by decreasing the induction period caused by oxygen.

Tsuji and coworkers[136] improved the elasticity, heat settability, and abrasion resistance of rayon as well as its adhesion to rubber by grafting on of butadiene, butadiene–styrene, or butadiene–acrylonitrile. The grafting also reduced the coefficient of friction of the fabric.

Cellulose Acetate. Cellulose acetate is relatively unstable toward radiation and adds vinyl monomers readily.[2–4] Therefore grafting studies of cellulose acetate are fairly extensive (see Table 2). Sensitizers have little effect on the rate or amount of grafting,[3] in contrast to cotton and rayon. Postirradiation studies[4] showed that oxygen decreases the number of available radicals in acetate yarn.

Hayakawa et al.[41,43] found that more homopolymer was formed by the mutual irradiation technique than by the preirradiation technique but that in the former case the cellulose acetate was grafted to a greater extent and the molecular weights of grafted polystyrene were higher (4.0×10^5 vs. 1.7×10^5). Matsuzaki, Komagata, and Sobue[87] found that the molecular-weight distribution of the grafted polystyrene is similar to that of ordinary radical-polymerized polystyrene and that termination occurs mainly by combination. Matsuda and coworkers[42,62] found that aromatic hydrocarbon solvents with large side chains markedly decreased the molecular weight of the grafted polystyrene and the percent grafting. Carbon tetrachloride also significantly decreased the graft molecular weights. Calculated transfer constants and activation energies were found to be in satisfactory agreement with those reported for homogeneous styrene polymerization.

Hayakawa, Kawase, and Matsuda[44] have reported the tensile properties of cellulose acetate–styrene grafted fibers. Rutherford and coworkers[3,4] found no marked changes in the physical properties of cellulose acetate caused by grafting on of any of a number of vinyl monomers (methyl acrylate, ethyl acrylate, acrylonitrile, butadiene, or acrylic acid–allyl acrylate). Ide et al.[52] compared the physical properties of graft copolymers of acrylic esters on cellulose acetate with those of blends of the polyacrylates and cellulose acetate. They found that, with increasing acrylic ester content, the elongation of the graft polymers increases while that of the blends remains unchanged. The microscopic texture of the graft copolymers was more homogeneous than that of the blends. Both polymers had two dynamic-loss peaks, corresponding to the peaks for cellulose acetate and polyacrylic ester. The dynamic elastic modulus of the grafted copolymers was always lower than that of the corresponding blend. Yasuda, Wray, and Stannett[149] prepared grafts of styrene and methyl methacrylate. They found that the behavior of the grafts was quite different from that of corresponding physical mixtures and that the graft copolymers were less soluble than either of the homopolymers. Hayakawa, Kawase, and Matsuda[44] have examined the tensile properties of cellulose acetate–stvrene grafted fibers.

Sumitomo, Takamuku, and Hachihama[129] studied the effect of solvents, styrene concentration, and degree of acetylation. They found that the rate of polymerization of styrene was increased by the presence of cellulose acetate. Benzene, which is not a solvent for cellulose acetate, increased the grafting efficiency as the dose rate was increased. However, for solvents such as acetone and formamide, the grafting efficiency decreased with increased dose rate. The increased efficiency with benzene was ascribed to easier diffusion of styrene to the grafting side, and the decreased efficiency in acetone and formamide to their chain-transfer ability. The efficiency of grafting reached a maximum at 54 to 55% acetylation. Measurements of the amount of styrene grafted on the ester groups by alkaline saponification followed by acetolysis indicated that when the mutual radiation technique is used, the selective grafting of styrene onto special sites of cellulose acetate is not favored.

Stannett, Wellons, and Yasuda[124] demonstrated that the yields and molecular weights of the polystyrene side chains were mutually dependent and governed by the interplay of diffusion-controlled growth and termination steps. A 50-fold increase in dose rate (mutual radiation technique) changed the rate of grafting only from 1.6 to 2.1%/hr at a film thickness of 0.025 mm. Reducing the thickness to 0.01 mm increased the rate of grafting at a high dose rate but reduced the yield per megarad. Pyridine was found to be a highly suitable grafting solvent because of a low radical yield. The proportions of grafted polystyrene attached to the polymer backbone and ester groups were determined by hydrolysis to be 77.6 and 22.4, respectively. These results are somewhat contrary to those of Sumitomo, Takamuku, and Hachihama.[129] Sobue et al.[122] grafted polystyrene on cellulose acetate films by a preirradiation technique using styrene in methanol solutions and, by infrared spectroscopy, identified the homopolymer produced outside and inside the films, the polystyrene grafted to acetyl groups (isolated by acid hydrolysis), and the polystyrene grafted to the backbone. Sobue et al. also reported in detail the relation of grafting conditions to the molecular weights of the grafted polymer, the degree of branching, and graft efficiency. They ob-

served that grafting occurred without the addition of methanol and was actually reduced until the level of about 70% methanol was reached, when grafting increased—presumably due to the gel effect. The graft yield was shown to follow the molecular weight of the grafted side chains by isolating the side chains by acid hydrolysis and measuring their molecular weight. Stannett[127] also examined in detail the grafting process of polystyrene onto cellulose acetate, including the role of concurrent radiation degradation. The structural details and properties of the pure isolated graft copolymers were determined. He observed that heterogeneously prepared grafts have extremely long chain lengths due to delayed termination. Wellons, Schindler, and Stannett[146] compared polystyrene–cellulose acetate graft copolymers prepared by preirradiation of cellulose acetate before addition of styrene–pyridine and by the mutual irradiation of the cellulose acetate and styrene–pyridine mixtures. The yield from the preirradiation process was two-thirds of that from the mutual process, although the products contained about the same percentage of polystyrene. The grafted side chains were separated by acid hydrolysis from the cellulosic backbone, and the resulting polystyrenes fractionated on a column. Both graft copolymers had unusually broad molecular-weight distributions. However, the mutual irradiation product had a broad single distribution with emphasis on the low-molecular-weight side, while the preirradiated product had a two-peak distribution with about 80% of the total weight being a very high molecular weight of very narrow distribution.

The unusually broad molecular-weight distributions are typical of a diffusion-controlled grafting process where the average chain length reached should depend on the distance of the growth site from the film surfaces. The development of a large amount of high-molecular-weight polymer of narrow molecular-weight distribution in the preirradiation process is probably due to the entrapment of a small proportion of the radicals in the crystalline regions and growth of these until chain termination by addition of solvent at the end of the experiment.

Wellons and Stannett[147] propose that cleavage of cellulose by gamma rays occurs after removal of a hydrogen at the 1, 4, or 5 position. In solution, cleavage may be forestalled by radical chain transfer to solvent molecules or by addition of monomer before cleavage can occur. To ascertain the ratio of side-chain formation to cleavage, the authors ran parallel experiments in the presence of styrene and of α-methyl styrene. The former forms graft copolymers; the latter adds to free-radical sites without further polymerization. The amount of grafted chains was determined from the molecular weight of the polystyrene liberated by hydrolysis of the grafted copolymer, and the amount of cleavage was estimated from a comparison of the molecular weights of the product irradiated in the presence of α-methyl styrene with that of the original cellulose acetate.

In pyridine solution there were 6.5 times as many side chains as cleavages; in swollen films there were 4 times as many. When the swelling solution (80 : 20 styrene : pyridine) was added after irradiation of the dry film, there was more cleavage than side chains. In this case the grafted products could be largely block copolymers. However, an estimated half of the grafted chains were attached to the ester groups of the cellulose acetate. This was shown by cold alkaline hydrolysis of the graft copolymers and subsequent extraction of the polystyrene with benzene.

POLYOLEFIN FIBERS

Polyethylene. While polyethylene has not achieved the prominence of polypropylene as a fiber, it is included in this review as it has served as a prototype for examining various factors that may affect grafting reactions—such as crystallinity (Refs. 36, 58, 59), orientation,[134,143] branching,[36,58] monomer effects (Refs. 78, 132, 143), kinetics,[32,59] and effects of polymer degradation.[134]

Lamb and Weale[78] studied the effect of pressure on graft copolymerization of vinyl monomers onto preirradiated polyethylene and found that the rate of grafting increases considerably with pressure in the heterogeneous system styrene–irradiated polyethylene up to about 3000 atm. At higher pressures the reaction was retarded; this was attributed to diffusion control of the propagation reaction. The rate of homopolymerization increases exponentially with pressure over the range 1 to 4000 atm. Unreproducible results were obtained using methyl methacrylate, due to lack of swelling of the substrate by this monomer. No grafting was observed with vinylidene chloride, *cis*- and *trans*-dichloroethylene, trichloroethylene, and tetrachloroethylene at pressures up to 5000 atm, presumably because of incompatibility of these monomers with polyethylene.

Wu et al.[148] studied the effect of preirradiation doses and antioxidants on radiation grafting to both polyethylene and polypropylene fibers; they proposed that Fe(II) ion retards the homopolymerization of vinyl monomers in the presence of these fibers by reducing to hydroxyl ions the hydroxyl free radicals that result from the decomposition of peroxides formed by irradiation in the presence of oxygen. The Fe(II) ion simultaneously causes a partial radical-chain destruction and reduction in the rate of grafting.

Polypropylene. Graft polymerization of vinyl monomers onto polypropylene fibers[3,4,132] apparently is not affected by sensitizers (e.g., H_2O, CH_3OH, or CH_3COOH) as might be expected, but is definitely affected by the polymer microstructure. The ease of grafting is a function of the degree of crystallinity.[38,94] The effect of orientation[134,138] has been mentioned previously.

Vlasov et al.[143] have probably grafted the greatest variety of vinyl monomers onto polypropylene. Umezawa and Hirota[140] grafted a large number of monomers, containing functional groups, as admixtures with other monomers, principally styrene, and also investigated[138,139] preirradiation in air as well as the liquid-phase grafting techniques using secondary alpha particles.

Because of the slow diffusion rates of most monomers in polyolefins, the grafting tends to occur mainly at the surface. Rutherford and coworkers[3,4] studied this aspect by means of dyed fiber cross sections. Matsuo, Iino, and Kondo[86] examined the transverse distribution of polystyrene grafts by microinterferometry and found that the distribution curves from the surface to the center of the specimens were catenary. Apparently the grafting was retarded in the vicinity of the surface when the grafting was performed at low dose rates or using thin films. They explained this effect by considering that, if the graft reaction was diffusion controlled, the grafting rate may be lower in the vicinity of the surface where the monomer concentration is higher, due to the Trommsdorff effect. Ódor and Geleji[94] found that at very high dose rates (120 krads/hr) the graft reaction on polypropylene films (with a 50% aqueous solution of acrylic acid) approached a constant value. At lower intensities a higher percentage of grafting could be obtained under the same irradiation and grafting conditions.

Torikai and Kubo[133] found that grafting of vinyl acetate induced cracks in the interior of polypropylene fiber, although styrene, methyl methacrylate, and acrylonitrile did not do so. The elongation of the polyvinyl acetate grafted fibers was also rapidly decreased with increasing grafting although that of the derivatives obtained by saponification was not. The thermal contraction was increased.

The dyeability of polypropylene can be improved by radiation grafting.[3,4,57,95] Rutherford and coworkers showed polypropylene fibers modified by grafting methyl acrylate, ethyl acrylate, and vinyl acetate[3,4] were dyeable with dispersed dyes by conventional procedures, but the wash fastness of the grafted and dyed materials was unsatisfactory.

No marked change in the physical properties of polypropylene were noted when polypropylene fibers were grafted with acrylonitrile, butadiene, and methyl and ethyl acrylate. The addition of relatively large amounts of methyl acrylate increased the melting point significantly, while small amounts of acrylonitrile caused a sharp increase in the melting point but did not affect the softening point.[3,4] No practical value was found for grafting as a method of improving the high-temperature behavior of polypropylene fibers.

WOOL AND SILK FIBERS

Except for a brief description of the effect of gamma radiation on silk,[4] there apparently has been no interest in modification of the properties of this fiber.

Grafting of acrylonitrile onto wool is accelerated in the presence of water, methanol, and acetic acid; with other monomers the effect is variable.[3,4] Horio, Imamura, and Mizukami[48] obtained efficient grafting of styrene and methyl methacrylate in acetone as well as in acrylonitrile–water solutions. They found that highly grafted fibers (140% graft by weight) lost their wool-like character, the elongation at break decreased markedly, and the fiber became brittle and harsh. Fibers carrying a moderate amount of graft polymer (up to 82% graft by weight) showed modified stress-strain curves with increased initial elastic modulus and stress at yield point; tensile strength in both the dry and wet states is improved, the supercontraction is reduced, and the high elongation properties of wool are retained.

Stannett and coworkers[128] found that water or methanol was necessary to successfully graft styrene onto wool and postulated that the additives function as swelling agents, enabling the monomer to diffuse to the active centers created in wool by the radiation. The grafting rates always went through a maximum and then leveled off to a slower rate. This is the result of a slow buildup of the radical population, which leads eventually to a diffusion-controlled rate of grafting. Considerable postpolymerization grafting also took place. Several allyl monomers, as well as acrylonitrile, were successfully grafted in the presence of water and methanol, but the degree of grafting depended on the amount of swelling agent present.

OTHER FIBERS

Armstrong, Walsh, and Rutherford[4] examined the effects of sensitizers on the grafting of a variety of monomers on an acrylic fiber. Like polyesters, acrylics are very stable toward radiation and show little tendency to undergo grafting.

Majumdar and Rapson[83] grafted styrene onto jute in the presence of a number of swelling agents by simultaneous and preirradiation techniques.

Schwarz and Roudeix[121] improved the dyeing characteristics of a polyvinyl chloride fiber by grafting on 4-vinyl pyridine. The depth of shade increased with grafting, and the high-temperature strength and dimensional strength were maintained, but bleeding and harshness of the fiber were noted. Iwakura et al.[57] improved the dyeability of a polyvinyl chloride fiber by both direct and acid dyes by grafting on glycidyl methacrylate and then reacting the epoxide groups with hydroxylamine.

Sakurada et al.[118] prepared graft copolymers on a polyvinyl alcohol fiber using butadiene–styrene, butadiene–acrylonitrile, styrene–acrylonitrile, and butadiene–styrene–acrylonitrile monomer mixtures.

Some Related Electron Spin Resonance Studies

The chemical reactions initiated by high-energy radiation involving organic molecules, while quite complex and still the subject of intensive study, seem to ultimately involve free radicals. Some recent data[30] indicate that all three types of species—cationic, anionic, and radical—can exist and react in very dry systems, but free radicals are the active species where either oxygen or moisture is present. Unsurprisingly, since these agents are usually present, there have been fairly extensive studies of G values (radicals per 100 ev of input energy absorbed) and of the lifetimes of free radicals induced in various fibers by high-energy irradiation using electron spin resonance (ESR) spectroscopy.

Bernard and Gagnaire[14,15] claim that gamma irradiation of cellulose (cotton linters) in air results in the formation of two types of radicals—type A, which is stable to water and effective in grafting (the presence of water is necessary for grafting to improve accessibility), and type B, which is unstable to water and therefore uneffective in graft copolymerization on cellulose. From the reactivity of the radicals and their ESR spectrums, Bernard and Gagnaire concluded that type A radicals were formed by detachment of hydrogen from C-2 or C-3 of a glucose residue and type B radicals by detachment of hydrogen from C-6.

Dilli and Garnett[31] investigated gamma-irradiated carbohydrates using ESR and found that mono-, di-, and polysaccharides give similar spectrums consisting of a 15- to 20-gauss doublet (except that lyxose and lactose gave 4-line spectrums), which they attributed to the ejection of a hydrogen atom from either C-1 or C-6.

Florin and Wall[35] irradiated purified cellulose with ^{60}Co gamma rays in vacuo and found that the yield of radicals detected by ESR was not affected by the crystallinity of cellulose but, in agreement with Bernard and Gagnaire, that the presence of water decreases the yield significantly. Kroh and Walicki[73] found that the presence of styrene graft does not change the shape of the ESR spectrum of gamma-irradiated cellulose. The maximum concentration of unpaired spins was approximately 10^{19} per gram after a dose of 4.4 Mrads. They state that the shape of the curve suggests an energy-transfer process in which the most significant effect of styrene appears at grafting levels of up to 20%.

Arthur and Mares[6] showed by ESR spectroscopy that the concentrations of free radicals initiated in cellulose molecules by gamma radiation from ^{60}Co are decreased by the presence of substituted benzoyl groups spaced at least as far apart as 70 to 80 A. They related this to the increased retention in breaking strength of fibrous cotton cellulose, on exposure to gamma radiation, found after substitution of benzoyl groups in the cellulose molecules.

Krasnansky, Parker, and Florin[70] employed ESR and optical spectroscopy to detect intermediates produced by gamma irradiation of a polyamide and to study the kinetics of the decay of the intermediates. Matthies, Schlag, and Schwartz[89] concluded from ESR signals that the red coloration produced by the action of high-energy radiation on polyamide fibers is due to the formation of free radicals associated with the oxamide group.

Araki, Campbell, and Turner[5] studied by ESR the free radicals formed by gamma irradiation of polyethylene terephthalate. They found a long-lived signal in an oriented sample, due to efficient radical trapping in the oriented, crystalline regions. They concluded that the radical

$$-CO-O-\dot{C}H-CH_2-O-CO-$$

is definitely formed with a G value of 0.02 and tentatively assigned the spectrum of a minor component to the free radical

$$-CO-\dot{C}_6H_3-CO-$$

Ermolenko, Potapovich, and Makatun[33] detected by ESR an accumulation of long-lived primary radicals, apart from any short-lived radicals, in gamma-irradiated cotton cellulose. Oxidation to monocarboxycelluloses gave an ESR spectrum with less intense side lines: the higher the carboxy-group content the greater the decrease in intensity of the ESR signal. (FEM)

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Gamma-Irradiation Facility of Kyoto University Institute for Chemical Research*

Abstract: The 2-kilocurie gamma-irradiation facility of the Kyoto University Institute for Chemical Research is described. An interesting feature of the design is the mechanism that transfers the ^{60}Co pencils that make up the source from the storage pool to the irradiation position one at a time.

The first multicurie gamma-irradiation facility in Japan was constructed in 1958. For 9 years it has been used for chemical, biological, and physical studies and applications; the results have been published in the Institute's Bulletin, which receives worldwide distribution, and in other journals. The facility described here† is still in active use, with no major changes since its installation. It consists basically of the radiation source, which is stored in a water-filled pit when not in use; a mechanism for transferring the source from the pit to the irradiation position; and a sample conveyor (Fig. 1).

Source

The ^{60}Co radiation source was fabricated by Atomic Energy of Canada Ltd. in the form of 40 pencils. Each pencil had an activity of 61.7 curies in June 1957 when manufactured, and the source had a total activity of 2100 curies in April 1958 when the facility was installed. Each pencil (Fig. 2) is made up of nine ^{60}Co slugs — 0.25 in. in diameter, 1 in. long, and individually encapsulated in aluminum — loaded in a stainless-steel tube. The nine slugs plus their aluminum jackets

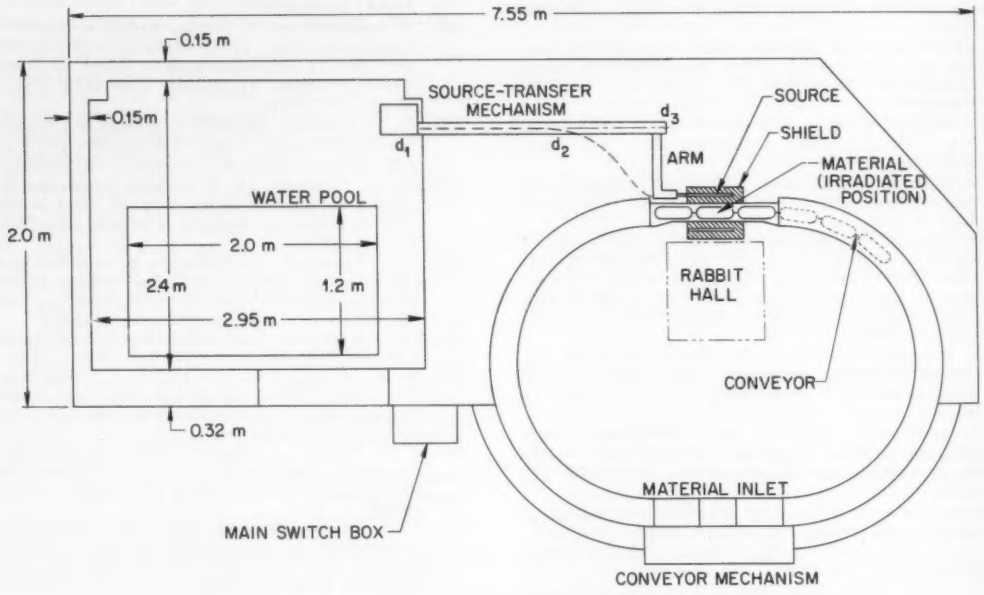


Fig. 1 Arrangement of 2-kilocurie irradiation facility.

give a useful pencil length of 10 in. or, with end-pieces, an overall length of 11.25 in. When in the irradiation position, the pencils are arranged in two concentric circles through the center of which pass the samples to be irradiated.

When not in use, the pencils are stored in a lead container in a water-filled pit. The pit, 2 by 1.2 by 2 m deep, is an extension of a water-filled pool, 2.9 by 2.4 by 1.2 m deep (Fig. 3).

*Based on "The 2-kilocurie ^{60}Co Gamma-Ray Irradiation Facility," by S. Okamoto, Y. Nakayama, and K. Takahashi, *Bulletin of the Institute for Chemical Research, Kyoto University*, 37: 299-305 (1959); "Gamma-Ray Dosimetry in an Irradiation Cavity of the 2000-curie ^{60}Co Facility" by S. Shimizu, S. Tanaka, and Y. Nakayama, *Bulletin of the Institute for Chemical Research, Kyoto University*, 37: 306-318 (1959); and letter of Nov. 30, 1966, from S. Shimizu, Director of Radioisotope Research Laboratory of the Institute. Dr. Shimizu kindly criticized this review before publication.

†Another 2-kilocurie facility particularly for biological and genetic studies is now nearing completion.

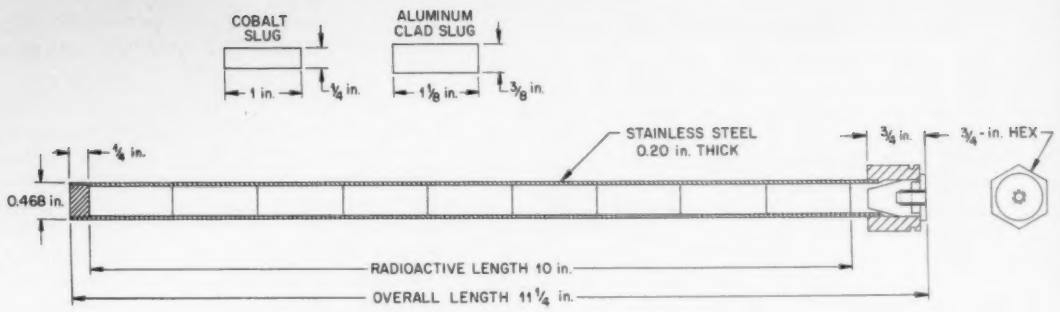


Fig. 2 Single ^{60}Co source pencil.

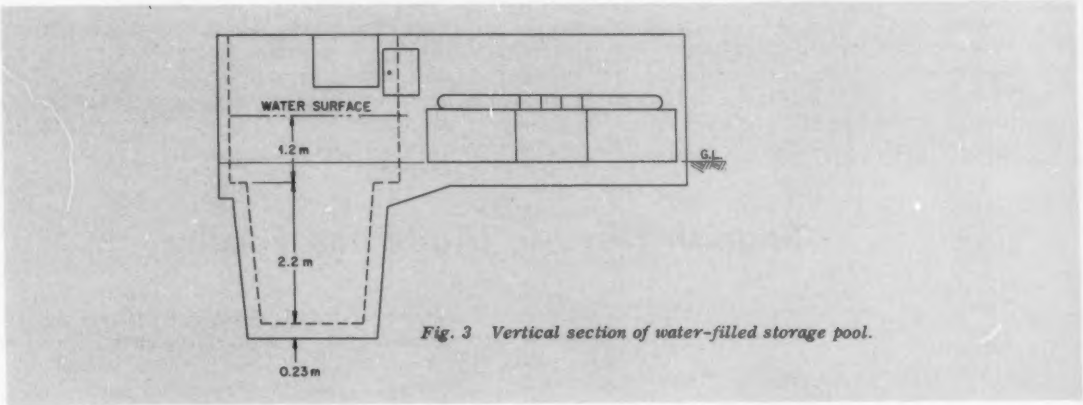
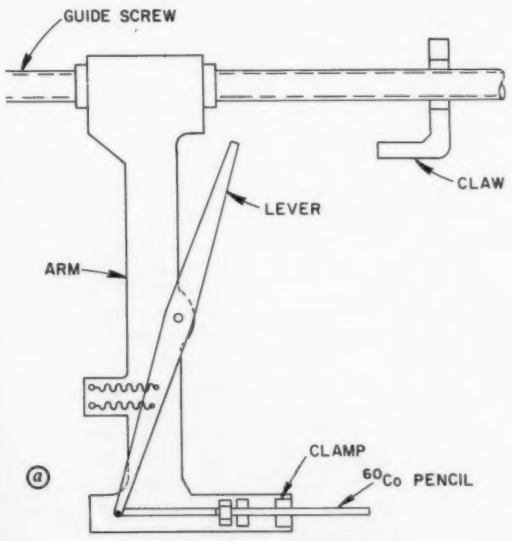


Fig. 3 Vertical section of water-filled storage pool.



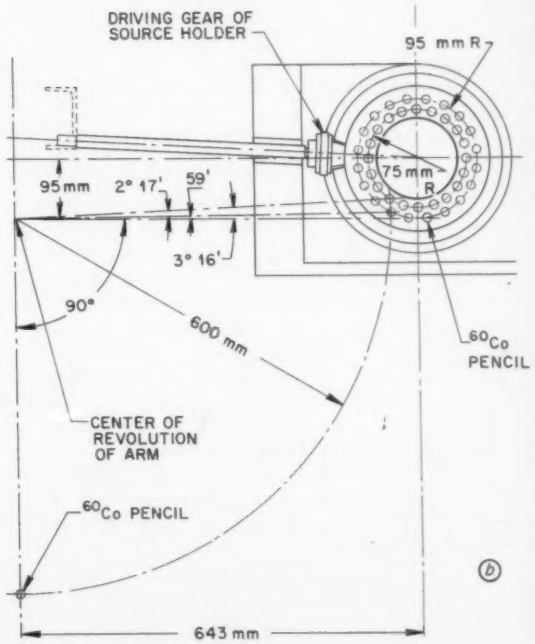


Fig. 4 (a) Source-pencil-transfer mechanism and (b) geometry of rotational movement of the arm.

Source-Charging Mechanism

When an irradiation is to be performed, the pencils are transferred one at a time from the storage pit to the irradiation position. A pencil is first picked up by a remote-controlled handling tool and placed in the clamp of the transfer arm (Fig. 4), which at that time is located at position d_1 in Fig. 1. The arm, with its pencil, is moved horizontally into the shielded transfer-mechanism tube by rotation of a guide screw driven by a motor in a box at d_1. During this step the pencil is moved entirely under water. When the pencil reaches position d_2, the arm starts to revolve around the guide screw so as to shift the pencil through a 90°59′ angle of the outer circle arrangement or a 93°16′ angle for the inner circle arrangement. When position d_3 is reached, the pencil is pushed into a hole in the source holder by means of the lever. The clamp, triggered by contact with the claw, opens to release the pencil, and the arm returns to the pool to pick up another pencil. The source holder is rotated to bring an empty tube into position for filling. When the facility is to be shut down, the cycle is reversed.

Sample Conveyor

Materials to be irradiated are loaded in an aluminum conveyor box at the front of the facility and moved through the conveyor tube to the source. The conveyor train has 28 boxes and can be moved either continuously or intermittently in either direction by means of a motor. A safety device prevents the driving motor from starting unless the loading port is securely closed.

Dose Rate

Dose rates in the irradiation cavity of the facility were estimated by both calculations and experimental use of ferrous sulfate dosimeters and silver-activated phosphate-glass needles. The dose rate at the center of the cavity was determined to be 234 kr/hr ± 5% in April 1958. (Martha Gerrard)

Spanish Náyade Irradiation Facility*

Abstract: The Spanish Náyade 7700-curie ^{60}Co irradiation facility is described.

The Náyade ^{60}Co irradiation facility (Fig. 1) is located in the Isotopes Section of the Chemistry and Isotopes Department at the Junta de Energía Nuclear site in Madrid. It was first used in February 1965, and since then studies on food irradiation, radiobiology, solid-state physics, plastic irradiation, and radiation chemistry in general have been conducted.

Source

The source, which is made of 12 ^{60}Co rods, was loaded with 4320 curies in December 1964; an additional loading in January 1966 gave a total activity of 7700 curies in May 1966. The theoretical capacity of the unit is 100,000 curies. Each rod has a 10-cm length of active material and is doubly encapsulated in stainless steel. The necks of the rods are made of magnetic stainless steel so that they can be handled by either an electromagnet or pincers. Material to be irradiated is placed inside a water-tight cylinder, which in turn is placed in the center of one of the supports for the rods. The supports (Fig. 2) hold the rods in circular arrays of 6, 13, or 28 cm diameter, and the change from one geometry to the other is made by moving the rods to another support. When all 12 rods are used, the radiation fields in the centers of the 6-, 13-, and 28-cm-diameter circles are 3.7, 1.1, and 0.35 Mr/hr, respectively. Isodose curves for one of the geometries used are shown in Fig. 3.

When special irradiation conditions are needed, fluids may be circulated through the cylinders, and approximate probes may be inserted for measurements during irradiation.

Irradiation Pool

The irradiation facility contains a water-filled pool, which is 4.2 m deep and 1.2 m on an edge and in which sources, cylinders, and supports are placed. All transfers of ^{60}Co are made at the bottom of the pool. The pool walls are of 20-cm-thick reinforced concrete, which is lined with an impermeable asphalt and then with brick. Stainless-steel rods are embedded in the walls and bottom of the pool for mounting any special device needed. Two watertight lights, 300 watts each, provide illumination. The pool curb is only 30 cm high to facilitate introducing the lead containers used in transporting sources. The lead carrier for the ^{60}Co rods, weighing 1500 kg, is handled with a crane.

The water in the pool, which acts as shield, must be very clear and pure. Purity is ensured by requiring a minimum resistivity of 4×10^5 ohms/cm and a *p*H between 5 and 7. For this reason a water purification system is an integral part of the irradiation facility. It uses both Dowex 21K and Dowex 50 ion-exchange resins and filters to remove dissolved and

*Based on an article (in Spanish) by E. Fornas Izquierdo, M. del val Cob, and F. de la Cruz Castillo, in *Energía Nuclear (Madrid)*, 10: 376-388 (1966); the authors kindly reviewed this summary before publication.

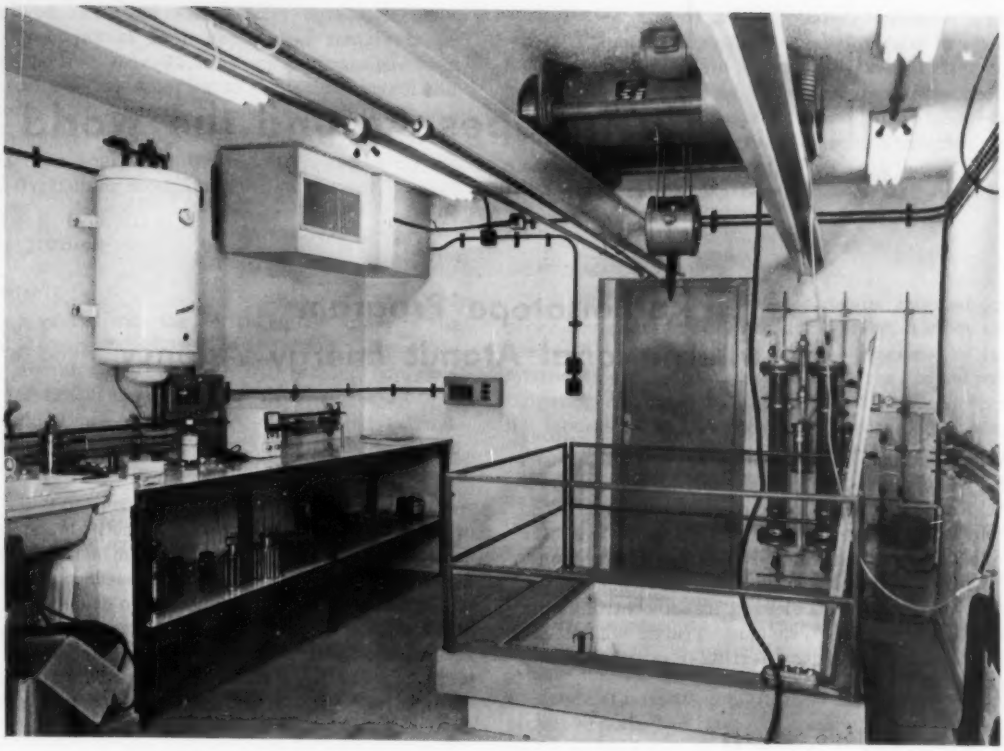


Fig. 1 Nâyade irradiation facility, showing water purification unit on the back wall and source-rod supports stored on the left.

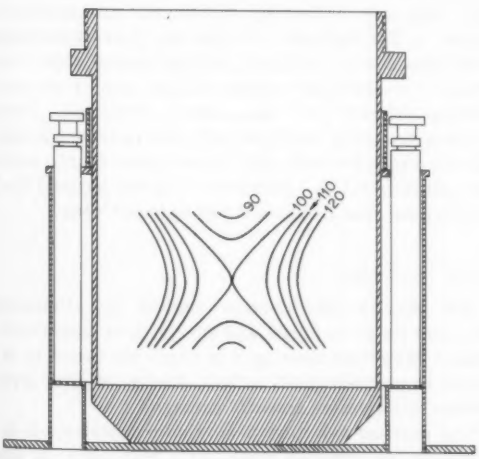


Fig. 2 Source-rod supports.

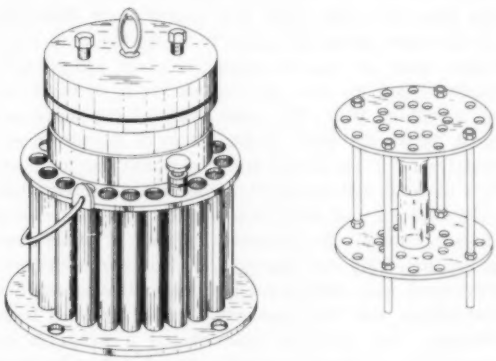


Fig. 3 Isodose curves of the Nâyade irradiation unit with ^{60}Co rods in 13-cm-diameter array. (Numbers are relative to 100% at the center.)

suspended materials from the water before it enters the pool.

There are two alarm systems to warn the operator of hazards from the two foreseeable risks: decrease in pool water level by damage to the water purification system and removal of a radioactive rod from the pool without adequate protection.

(Martha Gerrard)

Section

VI

Isotopes and Radiation Technology

Isotopes Around the World

Radioisotope Program of the International Atomic Energy Agency*

The International Atomic Energy Agency (IAEA) uses large radioisotope sources as well as tracers in its work. Among the programs currently being sponsored by the IAEA is the use of radioisotope sources for disinfestation of grain and processing of other foods, sterilization of pharmaceuticals and medical supplies, remote therapy of cancer, and insect control by the sterile-male-release technique. Tracer studies include those in hydrology, fertilizer utilization, and nutrition.

Large Radioisotope Sources

FOOD PROCESSING

A grain disinfestation program is under way in Turkey, where a 163-kilocurie ^{60}Co source has been installed in a commercial grain-handling terminal.† The plant is being built, at a cost of about $330,000, on the coast about 200 miles from the Syrian border. It can treat 30 tons of grain per hour, and the first results from its use are expected to be available by the middle of 1967. The IAEA believes that there is a great future for such plants all over the world, especially as it is slowly being realized that appreciable hazards are incurred in chemical disinfestation.

Such plants may also be useful for processing foods whose shipment is hindered by fear of virus contamination. Italy, for example, could import radiation-processed meat without fear of contamination and at a cost saving over what she now pays for live beef from Ethiopia. The IAEA is considering a program on processing of dried or smoked fish for the benefit of developing countries.

STERILIZATION OF PHARMACEUTICALS AND MEDICAL SUPPLIES

Considerable attention has been devoted to the use of radiation for sterilizing pharmaceuticals and medical supplies. A coordinated program set up with 14 member states is concerned with research to further this application and, particularly, to develop a "code of practice" for radiation sterilization that can be recommended for international acceptance. Laboratory work has been started to explore the feasibility of supplying needed biological tissues to hospitals from a central depository (tissue bank).

TELETHERAPY

In the IAEA's program on teletherapy, many physical data are collected, calculated, and published. Some of the subjects covered are dose distribution with high-energy radiation, isodose charts, depth-dose tables for medium-energy X rays, and single-field isodose charts for high-energy radiation. Three atlases are being published with all available information on radiation dose distribution important to medical physicists.‡ A "Radiation Data for Medical Use" service handles a thousand requests per year.

INSECT CONTROL

The sterile-male-release method has eliminated the fruit fly in Curaçao, and special irradiation techniques have been developed in which the insect is exposed to various gases before, during, or after irradiation to minimize somatic damage.

The method has also been shown applicable to insects whose females mate more than once. In this enormously widened field, work has been concentrated on the fruit fly, one of the most destructive insects of many tropical and subtropical fruits. For this insect

*Summary of "International Programs of the International Atomic Energy Agency" by H. Seligman, in Large Scale Production and Applications of Radioisotopes, Proceedings of the American Nuclear Society National Topical Meeting, March 21–23, 1966, Augusta, Georgia, USAEC Report DP-1066, Vol. 1, pp. III-57-62, Savannah River Laboratory, May 1966.

†See the article by Carden on this facility in Sec. IV of this issue.

‡Volume I, *Single-Field Isodose Charts*, by E. W. Webster and K. C. Tsien, was published in 1965; Vol. II, *Multiple-Field Isodose Charts*, by M. Cohen and S. J. Martin, in 1966.

the method has been successfully developed. Only minor problems of field application remain to be solved, and a 3-year $1.3 million program has been started in Central America to show that control and eradication of this fly are not only scientifically possible but also economical. Other insects to which the method may apply are the olive fly, tsetse fly, ox warble fly, codling moth, and rice stem borer.

Tracer Studies

HYDROLOGY

For 5 years, with the active collaboration of the World Meteorological Organization and various national laboratories, the IAEA has carried on a program for assessment of tritium in rainwater all over the world. Deuterium and ^{18}O are also determined. The data collected are being put on a computer, and already some unexpected results have been obtained on inflow of water into big basins or areas.

For the refinement of nuclear methods, experimental ^{14}C is being studied as a possible tracer.

MALNUTRITION

In studies on malnutrition, especially protein malnutrition, five projects have been selected as being particularly important in the study of protein metabolism: (1) standardization of labeled protein preparations used in turnover studies; (2) studies of protein deficiency in different geographical regions; (3) application of whole-body counting techniques to protein turnover studies; (4) data analyses in protein turnover studies; and (5) use of ^{3}H-labeled proteins in absorption studies. The albumin/globulin ratio has been found to vary greatly in persons at different sites and even to be reversed in a developed area compared to that in an underdeveloped one where protein foods may be limited. The funds needed for such a program are small, only $40,000 to $50,000 per year including the IAEA's laboratory expenses, consultants' meetings, research contracts, and technical assistance.

FERTILIZER UTILIZATION

In one of the most closely coordinated international programs ever achieved in agriculture, a study that uses radioisotopes to determine the efficiency of rice fertilization, the IAEA provides fertilizer to the participating countries and determines the ^{32}P and ^{15}N in its laboratories. The program is in its third year. The results obtained in various parts of the world are very similar and sometimes very surprising. For example, nitrogen utilization is best when the fertilizer is placed 5 cm below the surface, but for phosphorus, surface application is the most efficient method. Nitrogen uptake is not affected by the presence of phosphorus, but phosphorus utilization is slightly stimulated by the presence of nitrogen when both are placed at a 5-cm depth. In a similar program for maize, now in its second year, initial results indicate that the presence of nitrogen significantly increases the phosphorus uptake. The nitrogen of ammonium sulfate appears to be much more efficiently utilized when the fertilizer is applied close to tasseling time than when it is applied at planting time. (Martha Gerrard)

USAEC ADVISORY COMMITTEE ON ISOTOPES AND RADIATION DEVELOPMENT

Chope Fowler Landis Snyder Brantley English Stier
Stannett Conner Sharp Nason Artandi Kuranz Harmer

Section VII

Isotopes and Radiation Technology

Miscellaneous

Conferences

IAEA Symposium on Radioactive Dating and Methods of Low-Level Counting, Monaco

From March 2 to March 10, 172 experts from 30 countries gathered at Monaco to hear 65 papers presented from 14 countries and the International Atomic Energy Agency (IAEA) on radioactive dating and methods of low-level counting.

A feature of the conference was a historical review of radiocarbon dating by its inventor, W. F. Libby, who won the Nobel Prize for his discovery. Several papers pointed out that atmospheric carbon available to growing plants is strongly influenced by the world oceans since CO_2 in the atmosphere is in a state of equilibrium with the HCO_3^- ion of the oceans. The $^{14}C:{}^{12}C$ ratio is also influenced by temperature. H. E. Suess (USA) used this property to note that increased ^{14}C concentration represented periods of severe winters. Some notable winters must have occurred in the 24th and 26th centuries B. C.

M. S. Baxter (UK) used ^{14}C to check the age of Scotch whisky and said barley was an excellent measure of atmospheric ^{14}C activity via the spirits produced from it.

Other papers showed that explosions of nuclear devices have added a large amount of ^{14}C to the atmosphere. One paper established that the Industrial Revolution lowered the $^{14}C:{}^{12}C$ ratio because it added great amounts of natural carbon to the air from burning fossil fuels.

Suess (USA) and Münnich (Federal Republic of Germany) reported that in both the Pacific and Atlantic oceans the amount of ^{14}C decreases from north to south. S. M. Nakhla (France) used man-made ^{14}C to follow the decomposition of plants in the soil. He reported that formation of humic acid results after 4 to 5 years and that further decomposition into humin takes about 25 years. A study by J. Labeyrie (France) measured uptake of ^{14}C, ^{234}U, and ^{230}Th by coral in the Pacific to establish that the sea level has fluctuated more than 500 m in the last 500 thousand years.

In a summary of the discussions, P. E. Damon (USA) pointed out that many of the new discoveries were the result of the development of techniques for detecting very small quantities of radioelements. He termed these techniques "exquisite" and "delicate."

The proceedings of the symposium will be published by the IAEA later this year.

AEC Activities

Advisory Committee on Isotopes and Radiation Development Meets in Oak Ridge

On April 6 and 7 at the Oak Ridge National Laboratory, the AEC's Advisory Committee on Isotopes and Radiation Development held its 12th meeting since its establishment in 1958. The 19-member group, composed of representatives from government and industry, was set up to advise the AEC on ways to encourage wide-scale industrial use of radioisotopes and nuclear radiation. Committee members in attendance were J. L. Kuranz (Nuclear-Chicago Corp.), Chairman; J. W. Landis (Babcock and Wilcox Co.), Vice-Chairman; H. R. Chope (Industrial Nucleonics Corp.); V. T. Stannett (North Carolina State University); W. P. Conner (Hercules Research Center); R. A. Sharp (Beckman Instruments, Inc.); H. K. Nason (Monsanto Research Corp.); N. W. Snyder (Georgia Institute of Technology); Charles Artandi (Ethicon, Inc.); J. C. Brantley (Nuclear Science and Engineering Corp.); P. M. Stier (Union Carbide Corp.); and D. E. Harmer (Dow Chemical Co.). Representing the Washington AEC Staff were S. G. English, Asst. Gen. Mgr. for Research and Development; E. E. Fowler, Director, W. E. Mott, G. Y. Jordy, G. J. Rotariu, and D. S. Ballantine of DID; D. D. Mayhew, Office of the Controller; E. F. Greenleaf, Division of Production; Martin Moon, Division of Public Information; J. M. Prosser, Division of Reactor Development and Technology; J. A. McBride, Division of Regulation; and J. A. Powers, Space Nuclear Systems. H. M. Roth, D. C. Davis, R. B. Martin, and J. W. Nehls represented AEC's Oak Ridge Operations Office.

AEC Awards Contract to Arthur D. Little To Study Competition in Nuclear Industry

The Department of Justice is working with the AEC to enable both agencies to fulfill their responsibilities under the Atomic Energy Act and current antitrust legislation. To this end the AEC has chosen Arthur D.

Little, Inc., of Cambridge, Mass., to perform a study of competition in the nuclear industry.

For the study, only the nuclear power supply industry will be considered. This consists of all firms engaged in the business of supplying reactors, reactor components, nuclear fuel, or other products and services associated with the design, construction, and operation of nuclear electric plants. The study should provide guidelines for healthy and competitive development of the emerging nuclear industry.

James T. Ramey, AEC Commissioner, and Donald F. Turner, Department of Justice, will provide overall guidance to Arthur D. Little, Inc., during the study.

AEC Request for Meat Irradiator Proposals Brings 10 Responses

When the AEC asked for proposals to construct and operate a 1 million lb/year meat irradiator, it received no less than 10 responses. The contract should be let about June 1. The AEC is providing $270,000 in assistance, and the Department of the Army has guaranteed a 300 thousand lb/year base load for the first 3 years. The bidders, their associates, and the suggested sites are as follows:

Bidder	Associates	Site
AEL Food Automation Division	AEL Development and Research, Inc.; Radiation Facilities Inc.; Air Products & Chemicals Inc.; Radiant Energy Processing Corp.; and Radiation Consultants, Inc.	Camden–Philadelphia area
High Energy Processing Corp.	Hormel; Thermo-Bios Corp.; and Process Plants, Inc.	Bedford, Mass
Farmbest, Inc.	General Electric	Dennison, Iowa
Iso Nuclear Corp.	John Morrell & Co.	Buffalo, N. Y.
Rad-Mat, Inc.	Esskay; University of Maryland; and Food Technology Corp.	Gaithersburg, Md.
Applied Radiation Corp.	Holmes & Narver, Inc.; Atomic Energy of Canada Ltd.; Bridgeport Foods Corp.; King Meat Co.; San Jose Meat Co.; Safeway Stores; and Stater Brothers Markets	San Jose, Calif.
Houston Research Institute, Inc.	Henry House Packing Co. and Food Industries Research and Engineering Co.	Hanford, Wash.
General Radiation Corp.	None	Salt River Indian Reservation, near Phoenix, Ariz.
Irradiated Foods Inc.	Isotopes Inc.; Allen Products Co.; Martin-Marietta; and Uniroyal	Allentown, Pa.
Nuclear Materials and Equipment Corp.	Food Industries Radiation Council	Carroll, Iowa

Contracts Awarded To Study Isotope-Powered Cardiac Engine

Seven-month study contracts on the conceptual design of an isotopic engine to power a cardiac pump were awarded to Aerojet-General, San Ramon, Calif.; Donald W. Douglas Laboratories, Richland, Wash.; Thermal Electron Engineering Corp., Waltham, Mass.; and Westinghouse Astronuclear Laboratory, Pittsburgh, Pa. The program, cofunded by AEC's Division of Isotopes Development and NIH's National Heart Institute, involves a device, approximately 5 in. in diameter, which would be surgically implanted in the abdominal region to power an artificial circulatory-support system. The candidate isotopes, ^{238}Pu, ^{147}Pm, and ^{171}Tm, are the subject of a separate investigation being carried out by the AEC.

SIE and AEC Ask Private Industry To Register Radioisotope Research

Private industry is being urged to register current and planned research and development on isotopes and radiation with the Scientific Information Exchange (SIE) operated by the Smithsonian Institution. Working with the AEC and the AEC's Advisory Committee on Isotopes and Radiation Development, SIE has developed a category reporting system that is sufficiently informative but does not reveal proprietary information.

The SIE registers research on more than 95 thousand projects annually; the service answered some 50 thousand questions in 1966 and sent out over 750 thousand research résumés. Scientists, investigators, and research administrators of any recognized research organization can receive full information from SIE on all fields of basic and applied research.

One of the effects of the registry that is beneficial to both AEC and industry is the elimination or minimizing of overlapping research. This will make the overall isotope and radiation development program more effective and efficient.

Senator Talmadge and Representative Hagan Speak at Dedication of Grain Products Irradiator

On May 15, the world's first grain irradiator equipped to handle both bulk and packaged agricultural products was dedicated at Savannah, Ga. Senator H. E. Talmadge and Representative G. E. Hagan spoke at the luncheon given by the Southern Interstate Nuclear Board preceding the dedication. R. E. Hollingsworth, General Manager of the AEC, and G. L. Mehren, Assistant Secretary of the Department of Agriculture, spoke at the formal dedication.

The irradiator will demonstrate the use of radiation to disinfest agricultural products. It is located at the Stored-Products Insects Research and Devel-

opment Laboratory just outside Savannah. Grain disinfestation will be studied, and the possibility that radiation-resistant insect strains might develop will be investigated. Packaged commodities to be tested include flour, corn products, milled rice, breakfast cereals, cake mixes, dried fruits, nut meats, dry legumes, spices, dry animal feeds, peanuts, coffee, and cocoa.

Availability of Isotopes and Services

ORNL Stable-Isotope Inventory Augmented

Recent additions to the ORNL enriched stable-isotope inventory include the following:

Isotope	Purity, %	Amount available, g
^{35}Cl	99.3	27.0
^{92}Mo	98.3	67.0
^{110}Cd	96.7	2.0
^{142}Nd	97.7	36.0

General

New Company Offers Cesium and Cobalt Irradiators

Atomchem Corp. of Warren, Mich., is offering ^{60}Co- and ^{137}Cs-fueled irradiators for research, laboratory, and industrial applications. The company, which also distributes stable and radioactive labeled compounds and performs nuclear engineering design, is particularly interested in marketing its Rad-Lab line of extra-large-cavity irradiators, since comparable units are not offered elsewhere. The ^{60}Co device weighs approximately 27 thousand lb, and the ^{137}Cs device, approximately 16 thousand lb.

Aerojet-General Announces URIPS

An Undersea Radioisotope Power System (URIPS) is now available from Aerojet-General's Nuclear Engineering and Manufacturing Operations, San Ramon, Calif. The strontium-fueled thermoelectric generator weighs 800 lb and provides 1 watt of electricity. The URIPS will provide this power for 10 years and is designed to power undersea bench marks, wellhead markers, remote data links, and other similar devices at depths down to 20 thousand ft.

Atomic Radiation Used in the Battle of Capri

Israel and Italy are cooperating with the International Atomic Energy Agency and the Food and Agricultural Organization of the United Nations in a program aimed at ridding the island of Capri of the fruit fly. The sterile-male technique will be used.

Each week 4 million fruit-fly pupae will be bred in the Israel Institute of Biological Research at Nes-Ziona. The pupae will be sterilized at the Israeli Atomic Energy Commission's Soreq laboratory and then flown to Capri via Rome. On the island the flies will be released under the auspices of the Italian Atomic Energy Commission and the Italian Ministry of Agriculture. By competing with the fruit flies already there, the sterilized flies can markedly reduce the population of these destructive insects.

Capri is regarded as an important testing of the sterile-male technique. It offers an isolated environment in which results can be accurately judged on a weekly basis. The element of uncertainty is whether or not the pampered, sterilized, laboratory flies can survive air transport, live off the land, and compete successfully with the native flies. If the program goes as expected, by autumn there will be hardly any fruit flies left on the island.

New York State Industry Aided by Nuclear Science and Technology Information Center

The Western New York Nuclear Research Center has set up a Nuclear Science and Technology Information Center to aid New York State industry. Established under the State Technical Services Act, the new center will answer inquiries, provide state-of-the-art reports, and promote and publish symposia on nuclear information resources and radioisotope applications. The center hopes to set up training programs in radioisotope techniques and neutron activation analysis. Eventually the Nuclear Science and Technology Information Center intends to provide bibliographies of journal articles and government reports in its field on a monthly or semimonthly basis.

Selected Current Literature*†

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*International Atomic Energy Agency (IAEA) publications may be obtained from the National Agency for International Publications, Inc., 319 East 34th Street, New York, N. Y. 10016.

†All CFSTI reports are available for $3.00 (full size) and $0.65 (microfiche) from Clearinghouse for Federal Scientific and Technical Information, National Bureau of Standards, U. S. Department of Commerce, Springfield, Va. 22151.

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